STRUCTURAL AND SYNTHETIC STUDIES OF SOME PLATINUM AND PALLADIUM THIO-ACID COMPLEXES

by

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Thesis presented for the degree of
DOCTOR OF PHILOSOPHY
UNIVERSITY OF EDINBURGH
1975

SUMMARY

The dithioacid (1:1 dithiolato) complexes of nickel, palladium and platinum are briefly reviewed.

The compound $Pt(S_2PPh_2)_2$ (isomorphous with the nickel and palladium analogues) was prepared. The reaction of 1:1 molar ratios of tertiary phosphine with the chelate complex $M(S_2PPh_2)_2$ (M = Pd or Pt) gave the four coordinate complexes $M(S_2PPh_2)_2PR'_3$ by cleavage of a metal-sulphur bond in one chelate ring (PR'_3 = PPh_3, $PMePh_2$, PMe_2Ph, $PEtPh_2$). The metal atom is coordinated to the tertiary phosphine and to a bidentate and a unidentate S_2PPh_2 group. The analogous compounds $Pt(S_2PPh_2)_2AsPh_3$ and $Pt(S_2PPh_2)_2SbPh_3$ were also prepared. Excess of tertiary phosphine cleaved the remaining metal-sulphur bond in the unidentate S_2PPh_2 group giving the four coordinate ionic complexes $[M(S_2PPh_2)(PR'_3)_2]^+S_2PPh_2^-$. These ionic complexes are destabilised in non polar solvents and revert to $M(S_2PPh_2)_2PR'_3$ and free PR'_3. Ion exchange gave further complexes $[M(S_2PPh_2)(PR'_3)_2]X$ (X = Cl, BPh_4, PF_6). All the compounds were characterised by elemental analysis, i.r. and ^1H n.m.r. spectroscopy and by conductivity measurements.

The crystal structure of $Pd(S_2PPh_2)_2PPh_3$ was determined from X-ray Weissenberg data refined to an R factor of 0.112. The coordination about the palladium is close to square planar. The palladium is coordinated to the tertiary phosphine (Pd-P, 2.274 Å), to a bidentate dithioligand (Pd-S, 2.416 and 2.369 Å) and to a

unidentate S_2PPh_2 (Pd-S, 2.331 Å). The uncoordinated sulphur atom is at a distance 3.485 Å from the palladium atom.

Similar four coordinate complexes $M(S\text{-}S)_2PR'_3$ [$(S\text{-}S)^- = {}^-S_2CNEt_2$, ${}^-S_2CNMe_2$, ${}^-S_2COEt$, ${}^-S_2P(OEt)_2$; PR'_3 as above] were produced by reaction of 1:1 molar ratios of tertiary phosphine with $M(S\text{-}S)_2$. Variable temperature ^1H n.m.r. studies showed rapid room temperature exchange between the bidentate and unidentate ligands. As above four coordinate ionic complexes $[M(S_2CNR_2)(PR'_3)_2]^+S_2CNR_2^-$ (R = Me, Et; $PR'_3 = PMePh_2$) were obtained using excess tertiary phosphine, and further complexes $[M(S_2CNR_2)(PR'_3)_2]^+X^-$ ($X = ClnH_2O$, BPh_4, PF_6) were prepared by anion exchange. Variable temperature ^1H n.m.r. showed rapid room temperature equilibration between the $[M(S_2CNR_2)(PR'_3)_2]S_2CNR_2$ and $M(S_2CNR_2)_2PR'_3$ and free tertiary phosphine. The complexes $[M(S_2CNR_2)(PR'_3)_2]ClnH_2O$ were also isolated from interaction of the ionic dithiocarbamate species with chlorinated solvents. Attempted preparation of the ionic complexes $[M(S\text{-}S)(PR'_3)_2]^+(S\text{-}S)^-$ where $(S\text{-}S)^- = {}^-S_2P(OEt)_2$ and ${}^-S_2COR$ gave $M(PR'_3)_2S_2P(O)OEt$ and $M(PR'_3)_2S_2CO$ respectively. A mechanism for this reaction is presented which postulates the transient formation of the ionic species $[M(S\text{-}S)(PR'_3)_2]^+(S\text{-}S)^-$ and is supported by conductivity measurements and the isolation of the complexes $[M(S\text{-}S)(PR'_3)_2]^+BPh_4^-$ from the reaction mixtures.

The crystal structure of $Pt(S_2CNEt_2)_2PPh_3$ was determined

from X-ray Weissenberg data refined to an R factor of 0.100. The coordination about the platinum is close to square planar. The platinum is coordinated to the tertiary phosphine (Pt-P, 2.243 Å), to a bidentate dithiocarbamate (Pt-S, 2.298 and 2.335 Å) and to a unidentate dithiocarbamate (Pt-S, 2.328 Å). The uncoordinated sulphur is at a distance 3.449 Å from the platinum atom.

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A review of Dithioacid (1:1 Dithiolato) complexes of Nickel, Palladium and Platinum

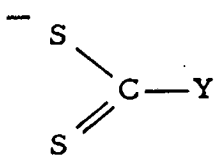
CHAPTER 1

Dithioacid (1:1 Dithiolato) Complexes of Nickel, Palladium and Platinum

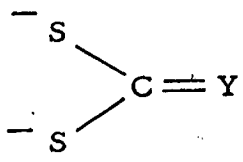
Since the work in this thesis is concerned with the preparation, properties and reactions of various palladium (II) and platinum (II) dithioacid complexes, a brief review of relevant earlier studies of dithioacid compounds of palladium, platinum and their lighter congener nickel is made in this introductory chapter.

Dithioacid complexes have been reported for a great number of metal ions. They have found extensive uses in analytical chemistry, as fungicides, pesticides, vulcanisation accelerators, high pressure lubricants, flotation agents and in many other applications.

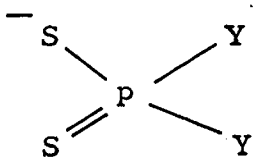
The 1,1 dithiolato ligands can be represented by the following diagrams:-



(I)



(II)



(III)

In type (I) are included the dithiocarbamates ($Y=NR_2$), the O-alkyl-dithiocarbonates (more commonly called the xanthates) (Y=OR), the thioxanthates (Y=SR), and the dithiocarboxylates (Y=R or Ar). Structure (II) includes the dithiocarbimates (Y=NR), the 1,1 ethenedithiolates ($Y=CR_2$), and the symmetrical trithiocarbonate ligand (Y=S). Ligands of type (III) comprise the dithiophosphates (Y=OR) and the phosphinodithioates (Y=R,Ar) and the difluorophos-phinodithioates (Y=F).

Several reviews of the ligands and their metal complexes have appeared [1-8]. Ligands of type (I) have been extensively reviewed by Coucouvanis [4], and the phosphinodithioates have been reviewed by Kuchen et al [7]. Very recently, a review of the dithiophosphates with some reference to related ligands has been published by Wasson et al [8]. Eisenberg has reviewed structural details of the 1,1 dithiolato complexes, based on X-ray studies [5]. Another useful summary of the structures of the bis chelate complexes is found in reference 6.

The divalent state is an important state for all members of the nickel triad (nickel, palladium, platinum). For nickel it is the most important oxidation state, but the second and third members of the group show the usual trend of increasing stabilisation of higher oxidation states, and many complexes of Pt(IV) (and to a much lesser extent of Pd(IV)) are known. Only the divalent state will be considered here.

Nickel (II) complexes exhibit a wide variety of structural forms. Six coordinate octahedral complexes are common, especially with neutral ligands such as amines. Both high and low spin trigonal bipyramidal and square pyramidal five coordinate complexes are known. Tetrahedral complexes are found particularly when the coordinating ligands are phosphines or halogens, but the majority of four coordinate complexes are square planar.

By contrast, the only important stereochemistry for complexes of platinum(II) and palladium(II) is the square planar form although a few five and six coordinate complexes are known. Frequently these

have been found where the ligand is multidentate, or of an unusual nature[9,10]. For instance, the series of compounds [M(L)X]Y, (M= Pd, Pt; L=tri(o-phenylarsinophenyl) arsine (QAS)[11,12], or the phosphorus analogue (QP)[13]; X=Cl, Br; Y=Cl, Br, BPh_4), are thought to exist in solution, and in the solid state, in a trigonal bipyramidal form as found in the crystal structure of $[Pt(QAS)I]BPh_4$[11]. Similarly five coordination, in a square pyramidal form, is found in $[Pd(TPAS)Cl]ClO_4, C_6H_6$ where (TPAS)=o-phenylenebis-(o-dimethylarsinophenylmethylarsine)[14]. X-ray studies of the $Pt(SnCl_3)_5^{3-}$ ion have shown a trigonal bipyramidal coordination by the monodentate $SnCl_3^-$ ligands[15], although it is thought that the coordination is different in solution. A five coordinate structure has also been suggested for some complexes of form $M(phos)_3X_2$ where M=Pd, Pt; X=Br, and where the tertiary phosphines are unusual in that the phosphorus forms part of a five membered ring in the phosphine[16]. Solution studies of halide addition to bis(diarsine)-palladium and platinum complexes have suggested the formation of five and six coordinated species[17]. The crystal structures of $M(C_6H_4(AsMe_2)_2)_2X_2$ (M=Pd, X=I[19]; M=Pt, X=Cl[20], I[18]) show a distorted octahedral structure with trans coordinated X ligands, but the M-X bonds are long (especially in the platinum complexes) suggesting that the structure is basically square planar with only weak metal-halide interactions.

In regular octahedral complexes the ligand arrangement around the central atom causes the E_g metal-ligand antibonding molecular

orbital pair called the '$d_{x^2-y^2}$ and d_{z^2}' orbitals for simplicity, to have higher energy than the remainder of the metal d orbitals. Thus octahedral d^8 complexes have two unpaired electrons in this top pair of molecular orbitals and are paramagnetic.

Tetragonal distortion of an octahedral complex eventually leads to a square planar configuration. There, the '$d_{x^2-y^2}$' orbital becomes very strongly antibonding while the d_{z^2} orbital drops in energy. The other d orbitals are also changed in energy and the d_{xy} orbital in fact rises in energy above the d_{z^2} orbital. Since there is then a large energy difference between the top two d orbitals, a d^8 square planar complex is invariably spin paired and diamagnetic.

It can be shown that there is a maximum overall decrease in d electron energy in going from an octahedral to a square planar complex for a d^8 electron configuration. Other factors affecting the total binding energy will include degree of overlap and energy compatibility between the metal and ligand orbitals, but these factors are not easy to quantify. The theoretical prediction is born out in practice as the members of the nickel triad show a great tendency to form square planar complexes in their +2 oxidation state. This tendency is especially marked in palladium and platinum, since the 4d and 5d orbitals are more outlying than the 3d orbitals, and are therefore more affected by the ligand approach, thus causing greater energy separation between the d orbitals. In addition, spin pairing is more favoured since the 4d and 5d orbitals are spatially greater.

Unlike the O and N donor ligands, the 1,1 dithiolates readily form

four membered chelate rings with a wide variety of transition metals of greatly differing oxidation and d-electron states. The resulting chelate ring is expected to be highly strained. The 1,1 dithiolato bis chelates of nickel(II) first reported by Delépine[21], Cambi[22] and Malatesta[23] have been studied extensively. Magnetic susceptibility measurements of the bis dithiocarbamates first indicated that the coordination was square planar[24] and the first X-ray structure by Peyronel on $Ni(S_2CN^nPr_2)_2$ confirmed the square planar, monomeric structure[25]. Subsequently, the bis chelates of nickel(II) have formed the basis for numerous X-ray structure determinations. In particular the structures of the dithiocarbamates have been studied exhaustively, since minor alterations of the terminal alkyl groups produced markedly varying biological activity, but with one exception[26], all the $Ni(S\text{-}S)_2$ complexes (S-S=1,1 dithiolato ligand) have distorted square planar geometry, and the palladium and platinum complexes have usually been found to be isomorphous with the corresponding nickel complex[5]. The chief distortion from square planarity in all the complexes is due to the small S-Ni-S angle, caused by the chelate ring formation. In complexes of ligand type (I) and (II) the strain is particularly great, the average S-Ni-S angle being 79°. In the dithiophosphates and phosphinodithioates the S-Ni-S angle of 88° is much closer to an undistorted square planar angle, but the chelate ring is still strained as is shown by the small S-P-S angles.

The sigma bonding is normal for square planar complexes. Each

sulphur atom can be considered to be sp^2 hybridised, and thus can contribute a lone pair into the metal molecular orbitals (Figure 1.1a). It can also be seen from Figures 1.1b, c, d that an extensive π-system within the ligand is possible involving overlap of the sulphur $3p_z$ and carbon $2p_z$ orbitals in ligands of type (I). A similar π-system involving some combination of the phosphorus $3p_z$ and 3d orbitals is also possible in ligands of type (III). Even more extensive π-overlap is possible in ligands of type (II) and for some ligands of type (I) involving ligand atoms beyond the chelate ring (Figures 1.1e, f, g).

Evidence for electron delocalisation over the chelate ring is shown by the equivalence of the M-S bonds, and also of the S-C bonds (average 1.70 A^o) for ligands of types (I) and (II), or S-P bonds (average 1.90 A^o) for ligands of type (III). In addition, these latter S-X bond distances (X=C or P) are intermediate between the usual single and double bond lengths[5].

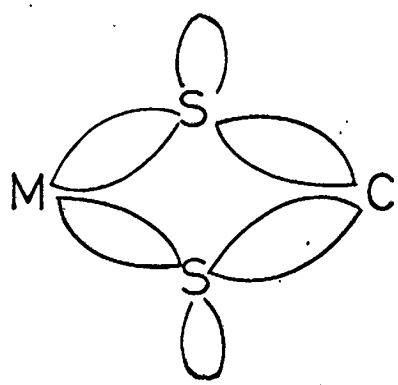
Evidence that the π-system extends beyond the S-X-S group for ligands of type (II) (Figures 1.1e, f, g) is shown in the equivalence of all the C-S bonds (1.69 A^o) in $Ni(S_2CS)_2^{2-}$ where the usual square planar coordination is found[27].

Infrared studies of the bisdithiocarbamates and bisxanthates of nickel[28,29] indicated that electron delocalisation beyond the chelate ligand atoms was present in the dithiocarbamate complexes, but not in the xanthates. X-ray studies later showed that the C-N bond distances in the dithiocarbamates were intermediate between single and double bond lengths[5], while the C-O bond length in $Ni(S_2COEt)_2$[30]

FIGURE 1.1

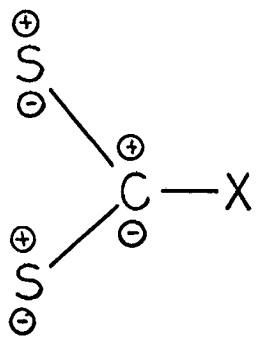
Molecular orbitals in dithio-ligand complexes

Ligand σ-system

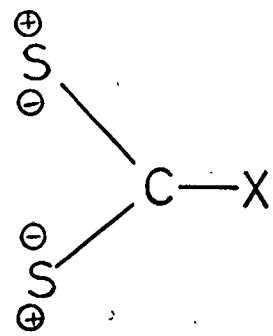


(a)

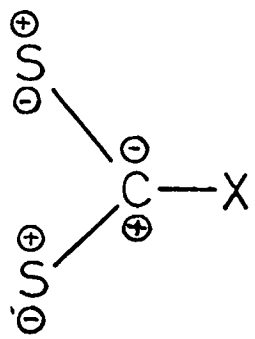
Ligand π-system



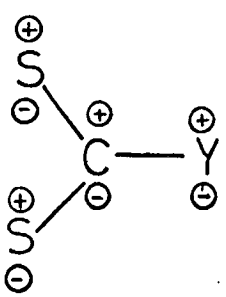
$1\pi_v$ (b)



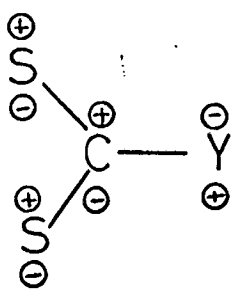
$2\pi_v$ (c)



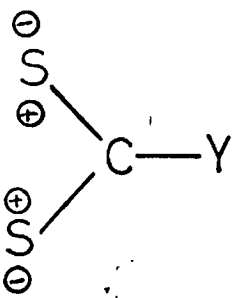
$3\pi_v$ (d)



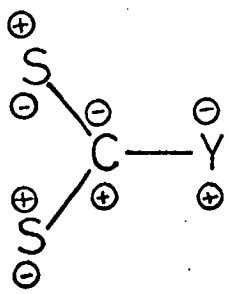
$1\pi_v$ (e)



$2\pi_v$ (f)



$3\pi_v$ (g)



$4\pi_v$ (h)

is close to that normally found for a single bond. It would appear that in the dithiocarbamates, the $2p_z$ orbitals of nitrogen are of suitable energy to overlap with the chelate system, while those of oxygen in the xanthate complexes are of too low energy.

From the diagrams it can be seen that the ligand π-orbitals are of suitable symmetry to overlap with metal π-orbitals. In a d^8 square planar configuration no empty metal d orbitals are available for overlap with the full ligand π-orbitals, but the empty metal p_z orbital is of the correct symmetry to overlap with the ligand $1\pi_v$ orbital (Figure 1.1b) or $1\pi_v$ or $2\pi_v$ orbitals (Figures 1.1e, f). It would appear that there is significant overlap between the $1\pi_v$ orbital and the metal p_z orbital in ligands of type (II) and the dithiocarbamates, but that the $1\pi_v$ orbital in other ligands of type (I) (and most likely the $2\pi_v$ orbital in ligands of type (II)) are of too high energy for appreciable overlap. The sulphur 3d orbitals and the empty $3\pi_v$ or $4\pi_v$ (Figures 1.1d, g) are of correct symmetry for overlap with the full metal orbitals but it has been suggested that this is of small importance in these complexes[5].

Unusual structures have been found for $[Ni(S_2CCH_2Ph)_2]_2$[26] where there are four bridging ligands similar to that found for bis(monothiobenzoato)nickel[31], and in $[Pt(p\text{-dithiocumato})_2]_2$[32] where there are two bridging and two chelate dithio-ligands. Both complexes show significant metal-metal interactions.

Interactions of metal complexes with Lewis bases may cause increase in the metal coordination number. While nickel complexes

react readily with nitrogen donors, palladium and platinum show a much greater tendency to form complexes with heavy atom donors (such as P, As, S) since the possibility of metal→ligand π-interaction becomes important for the more outlying 4d and 5d orbitals.

The reactions of $Ni(S\text{-}S)_2$ complexes with amines have been widely investigated. The reactivity of the 1,1 dithioacid bis chelates of nickel(II) varies substantially, and is thought to depend on the electron density in the metal p_z orbital from electron donation by the ligand orbitals, as this will decrease the availability of the p_z orbital for apical interaction with bases [40]. Thus complexes of ligand type (II), and those of type (I) which form extended π-orbital systems involving atoms beyond the S-C-S group, show less reactivity towards bases; the nickel bis(trithiocarbonate) ion does not react with bases, the dithiocarbamates show intermediate reactivity, and the xanthates where little electron delocalisation outside the S-C-S moiety occurs, react readily, as do the ligands of type (III).

Jørgensen first obtained bis pyridine adducts with $Ni(S_2P(OEt)_2)_2$ and $Ni(S_2COEt)_2$ [33]. From the electronic spectra, an octahedral structure containing <u>trans</u> coordinated pyridine molecules was postulated. Subsequently complexes of stoicheiometry $Ni(S\text{-}S)_2 2B$ (B=pyridine, 4-methylpyridine, 3-methylpyridine) have been prepared for $^-S\text{-}S = {}^-S_2P(OR)_2$ [44,42,39,34], $^-S_2PR_2$ [37], $^-S_2COEt$ [33,35,41], ^-S_2CSR [38]. No reactions with the dithiocarbamate nickel chelates were obtained except for $Ni(S_2CNH_2)_2$ and

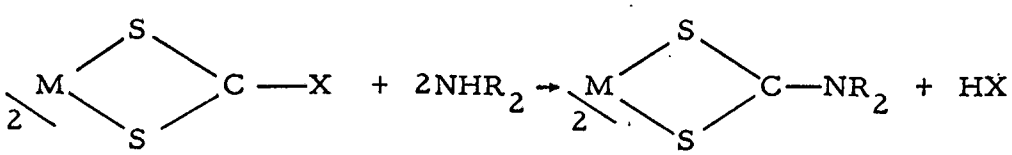
$Ni(S_2CNH(p\text{-}ClC_6H_4))_2$[35] where the $1\pi_v$ orbital might be less favoured. The octahedral structure has been confirmed by the crystal structures of $Ni(S_2PPh_2)_2py_2$[46] and $Ni(S_2P(OEt)_2)_2py_2$[45]. The structures are closely similar, and show single Ni-N bonds in the apical positions. The NiS_4 group is planar, but the Ni-S bond and the S-P-S angle are increased with decrease of the S-Ni-S angle.

With bidentate bases, complexes of form $Ni(S\text{-}S)_2B_2$ are obtained (B_2=1,10 phenanthroline, 2,2' bipyridyl, $^-S\text{-}S^-S_2P(OEt)_2$, $^-S_2COEt$)[33,34]. In these complexes cis coordinated nitrogen atoms are necessary in the octahedral products. The cis configuration has been confirmed by X-ray studies of $Ni[S_2P(OMe)_2]_2bipy$[47], $Ni[S_2P(OMe)_2]_2(phen)$[48] and $Ni[S_2P(OEt)_2]_2(phen)$[49].

Electronic spectral studies suggested that the base addition proceded in a stepwise manner to give 1:1 adducts, which were thought to have five coordinate square pyramidal structures, and then the trans octahedral 2:1 adducts[37]. Secondary alkylamines[34,41,42,44] and α-substituted pyridine derivatives[41,42,44] are thought to give only the five coordinate adducts, possibly due to steric effects. In support of this, the crystal structure of $Ni(S_2PEt_2)_2$ Quinoline reveals a five coordinate square pyramidal structure[48]. The nitrogen atom occupies the apical position and the nickel atom is slightly above (0.52A°) the basal plane of the four sulphur atoms. Besides adduct formation, complete cleavage of the Ni-S bonds appears to occur when an excess of 1,10 phenanthroline is added to $Ni[S_2P(OR)_2]_2$ giving the octahedral product $[Ni(phen)_3][S_2P(OR)_2]_2$[48b].

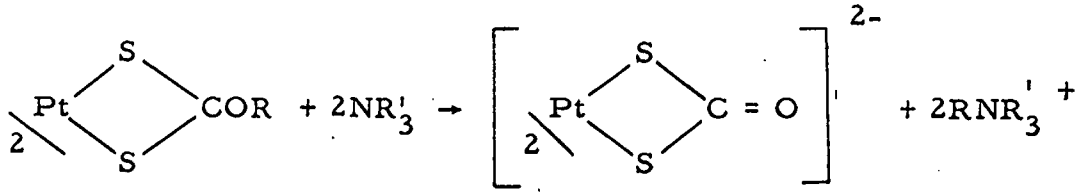
For palladium, the reaction between $Pd[S_2P(OEt)_2]_2$ and $BuNH_2$ is briefly reported to give a solid product, but no platinum amine adducts have been obtained[39].

Besides attack at the metal, secondary saturated amines may also cause nucleophilic attack of the CS_2 carbon atom with cleavage of the C-X bond and formation of a dithiocarbamate metal chelate as illustrated in equation (1) (M=Ni, X=NH_2, amine=piperidine or morpholine[35,36]; M=Ni, X=OR, amine=piperidine, 4-methylpiperidine; M=Pt, X=OCH_2Ph, amine=4-methylpiperidine[36,40]).



(1)

A similar reaction has been found to occur for $[Ni(SCH_2Ph)(S_2CSCH_2Ph)]_2$ with secondary amines, giving the corresponding dithiocarbamate complex by cleavage of the thioxanthate C-S bond[40]. It has also been suggested that the reaction of $Pt(S_2COCH_2Ph)_2$ with quinuclidine produces cleavage of the C_2-O bond of the xanthate as shown [equation (2)] which provides a possible explanation for the formation of the observed quaternised nitrogen species[40].



(2)

Few reactions of the nickel bischelates with tertiary phosphines have been reported. The 1:1 adduct of $Ni[S_2P(OEt)_2]_2$ with PPh_3 has been postulated to have a square pyrimidal structure from i.r. and u.v. spectral studies[41b], and solution studies have indicated the existence of $Ni(S_2COEt)_2PPh_3$[41a].

By contrast, tertiary phosphines are found to coordinate readily to the palladium and platinum 1,1 dithiolates. Fackler first reported the reaction of tertiary phosphines with $M(S\text{-}S)_2$ (M=Pd, Pt) complexes[50, 51]. Thus, 1:1 molar ratios of methyldiphenylphosphine were found to react readily for $^-S\text{-}S = {}^-S_2COR$, $^-S_2P(OEt)_2$, ^-S_2CR, but only a slow reaction with $Pt(S_2CNEt_2)_2$ was reported. Spectrophotometric titration of the reaction with $Pt(S_2COCH_2Ph)_2$ with PPh_3, and isolation of crystalline products of stoicheiometry $M(S\text{-}S)_2PMePh_2$ (M=Pd, $^-S\text{-}S={}^-S_2P(OEt)_2$, $^-S_2COEt$; M=Pt, $^-S\text{-}S=$ 3,4,5 trimethoxydithiobenzoate, p-dithiocumate (or 3-isopropyl dithiobenzoate)) indicated that a 1:1 adduct of form $M(S\text{-}S)_2PR_3$ was formed in all the reactions. The ^1H n.m.r. spectra in CS_2 were consistent with metal-phosphine coordination. Variable temperature ^1H n.m.r. studies of the methyl resonance of the dithio-ligands of $Pt[S_2P(OEt)_2]_2PMePh_2$ and $Pt(S_2CNEt_2)_2PMePh_2$ in CS_2 led to the proposal that all the complexes of this type were five coordinate species in solution. At room temperature rapid equilibration between a five coordinate trigonal bipyramidal structure and a solvated square pyramidal structure was thought to occur, with the latter structure being the preferred low temperature form. The

possibility of equilibration between a square planar open chelate ring complex and a trigonal bipyramidal five coordinate species, with the former as the preferred low temperature form, was also considered. However, the observed equivalence of the dithio-methyl groups in the dithiocarbamate complex, together with the facile platinum-phosphorus bond cleavage and exchange which was observed in all the $Pt(S\text{-}S)_2PR_3$ complexes, appeared to make this unlikely (but see further work in Chapters 4 and 5).

The reaction of excess $PMePh_2$ with Pt(p-dithiocumato)$_2$ or Pt(3,4,5-trimethoxydithiobenzoato)$_2$ gave products which were thought to be possibly six coordinated 2:1 adducts, and this was taken as further evidence of a stepwise reaction proceding via the five coordinate 1:1 adduct. The reaction of excess tertiary phosphine with $M(S_2CS)_2^{2-}$ however, was reported to give cis $(PR_3)_2MS_2CS$ with complete cleavage of the chelate dithioligand [40]. Furthermore, the reaction of excess tertiary phosphines with $M(S\text{-}S)_2$ (M=Pd, Pt; $^-S\text{-}S^-=^-S_2COEt$, $^-S_2COCH_2Ph$) in $CHCl_3$ was reported by Fackler to give the novel products $(PR_3)_2MS_2CO$ ($PR_3=PPh_3$, M=Pt; $PR_3=PMePh_2$, M=Pd, Pt) and an organic product $R\text{-}S_2COR$ (R=Et, CH_2Ph). No overall reaction mechanism was proposed but nucleophilic attack by the sulphur atom of one xanthate complex on the C_2 carbon of another molecule was thought to be an important step in the reaction. A similar product was obtained with $M[S_2P(OEt)_2]_2$ giving $(PR_3)_2MS_2\text{-}P(O)OEt$ [40] (see further work in Chapter 4).

Finally, Stephenson and Faithful independently investigated the

reaction of bis(diphenylphosphinodithioato)palladium(II) with tertiary phosphines, and obtained the products $Pd(S_2PPh_2)_2PR_3$ (PR_3=PPh_3, $PEtPh_2$, PMe_2Ph, PEt_3) with 1:1 molar ratios of tertiary phosphines, and the complexes $Pd(S_2PPh_2)_2(PR_3)_2$ (PR_3=PMe_2Ph, PEt_3) with excess phosphine. By analogy with Fackler's conclusions and by an interpretation of the infrared spectra, these complexes were assigned as five and six coordinate species also [52].

CHAPTER 2

Palladium(II) and Platinum(II) complexes of Diphenylphosphinodithioic acid

CHAPTER 2

Palladium (II) and Platinum (II) Complexes of Diphenylphosphinodithioic acid.

2.1 Introduction

Studies of the reactions of bis(diphenylphosphinodithioato) palladium (II) with tertiary phosphines by Stephenson et al.[52] showed that two series of crystalline tertiary phosphine adducts were produced. The complexes obtained with 1:1 molar ratios of tertiary phosphine were of stoicheiometry $Pd(S_2PPh_2)_2PR_3$ (PR_3= PPh_3, $PEtPh_2$, PMe_2Ph, PEt_3) and were thought to contain five-coordinated palladium (II). Those obtained with an excess of tertiary phosphine, of stoicheiometry $Pd(S_2PPh_2)_2(PR_3)_2$ (PR_3= PMe_2Ph, PEt_3),were assigned a six coordinate structure. The isolation of palladium (II) complexes in these rare stereochemistries made an investigation of the analogous platinum system of considerable interest. Fackler's studies of tertiary phosphine reactions with $M(S\text{-}S)_2$ (M=Pd, Pt; $^-S\text{-}S^-=^-S_2COR$, $^-S_2P(OEt)_2$, ^-S_2CR)[40, 50, 51] had also indicated the possible formation of five coordinate species of stoicheiometry $M(S\text{-}S)_2PR_3$ with 1:1 molar ratios of tertiary phosphine. In most cases, the reaction with excess phosphine appeared to attack the ligand, but a brief mention was also made of the precipitation from solution of what may be six coordinate species, when excess of $PMePh_2$ was added to platinum (II) complexes of ring-substituted dithiobenzoates[50, 51].

2.2 Preparation of $Pt(S_2PPh_2)_2$

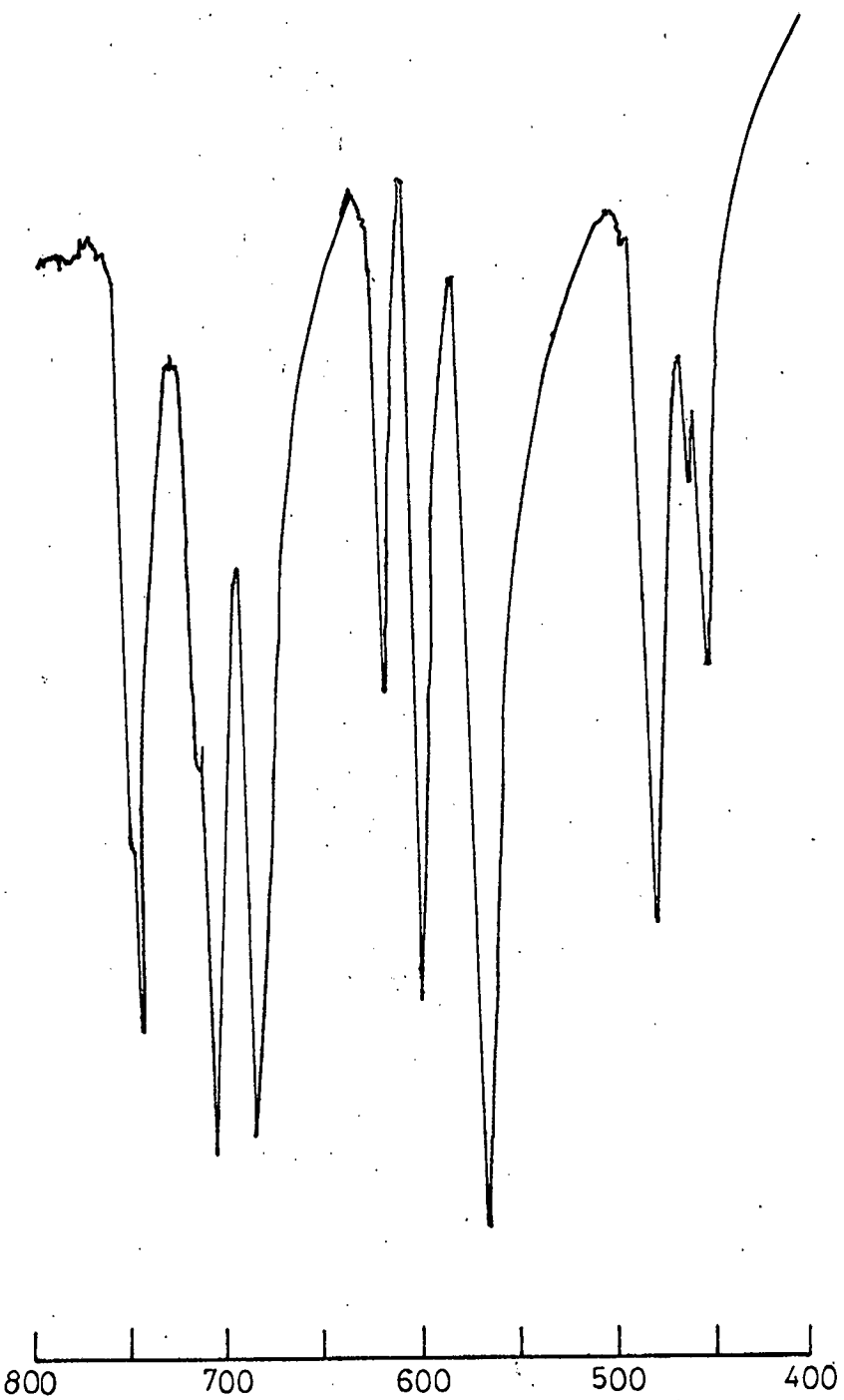
Bright orange crystals of $Pt(S_2PPh_2)_2$ were obtained by treatment of either K_2PtCl_4 or $[Pt(OAc)_2]_3$ with an excess of diphenylphosphinodithioic acid $[HS_2PPh_2]$. Like the analogous palladium complex[52], $Pt(S_2PPh_2)_2$ was insufficiently soluble in chloroform or benzene for a molecular weight determination to be made, but the mass spectra of the nickel, palladium and platinum complexes showed the maximum m/e values expected for monomeric structures. Comparison of the X-ray powder diffractometer measurements of the palladium and platinum complexes with that of the nickel complex (previously shown to be a square planar monomer by X-ray methods[53]) indicated that all three complexes were isomorphous. All the compounds were non-conducting in dichloromethane and showed identical i.r. spectra in the region 800-400 cm^{-1} (Figure 2.1).

2.3 Reaction of $M(S_2PPh_2)_2$ with tertiary phosphines (1:1 molar ratios)

Reaction of a suspension of $Pt(S_2PPh_2)_2$ in benzene with tertiary phosphines (1:1 molar ratios) rapidly gave bright yellow solutions from which lemon-yellow compounds of stoicheiometry $Pt(S_2PPh_2)_2PR_3$ were isolated, either by precipitation with light petroleum or by removal of the solvent under reduced pressure (PR_3=PPh_3, PPh_2Me, PMe_2Ph). A similar treatment of the red crystals of $Pd(S_2PPh_2)_2$ in benzene suspension gave orange crystals of $Pd(S_2PPh_2)_2PR_3$ where PR_3=PPh_3, PMe_2Ph, $PEtPh_2$ and PEt_3 as

FIGURE 2.1

I.r. spectrum of $Pt(S_2PPh_2)_2$ (Nujol Mull) 800-400 cm^{-1}



previously reported[52], and also for PPh_2Me and $P(n\text{-}Bu)_3$. However, when $P(n\text{-octyl})_3$ was reacted with $M(S_2PPh_2)_2$, or $P(n\text{-}Bu)_3$ with $Pt(S_2PPh_2)_2$, only sticky impure products were isolated. The PPh_3 complex could also be prepared by treating cis $Pt(PPh_3)_2Cl_2$ in benzene with an excess of HS_2PPh_2.

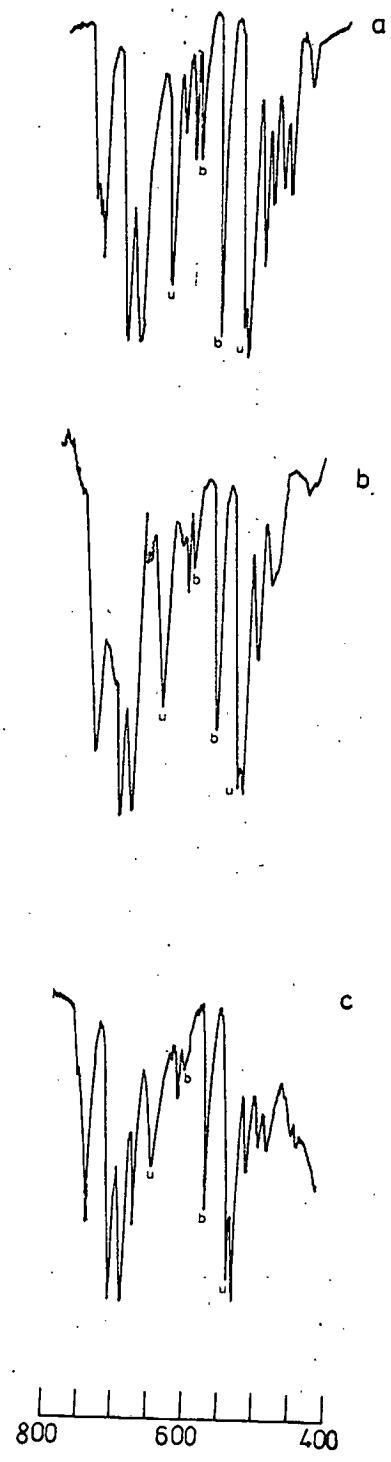
Molecular weight measurements in chloroform were consistent with monomeric complexes of form $M(S_2PPh_2)_2PR_3$ (M=Pd, Pt); and conductivity measurements showed the complexes were non-conducting (Table 2.2).

The i.r. spectra (in the region 800-400 cm^{-1}) were very similar for both the platinum and palladium complexes, apart from the differing tertiary phosphine vibrations. The i.r. spectra of all the diphenylphosphinodithioato-compounds in this region are complex due to the presence of both the ligand phenyl and phosphorus-sulphur vibrations (see Figures 2.2 and 2.3). Widely differing values have been reported for the ν(P-S) vibrations[7,54,55]. The mode of bonding of the diphenylphosphinodithioato-ligand to palladium in the tertiary phosphine complexes was initially inferred from the position and separation of two vibrations which were taken as the asymmetric (ν_1) and symmetric (ν_2) PS_2^- stretching vibrations, by analogy with empirical rules derived for acetate complexes[52]. However, in contrast to the ^-OCOMe ion, for the $Ph_2PS_2^-$ group several other vibrations of similar energy to ν_1 and ν_2 are also of the same symmetry group. Extensive coupling of the vibrations is therefore probable which invalidates arguments based on the

I.r. spectra of $Pt(S_2PPh_2)_2PPh_3$ (800-400 cm^{-1})

u = characteristic unidentate vibration

b = characteristic bidentate vibration



bright yellow form
(nujol mull)

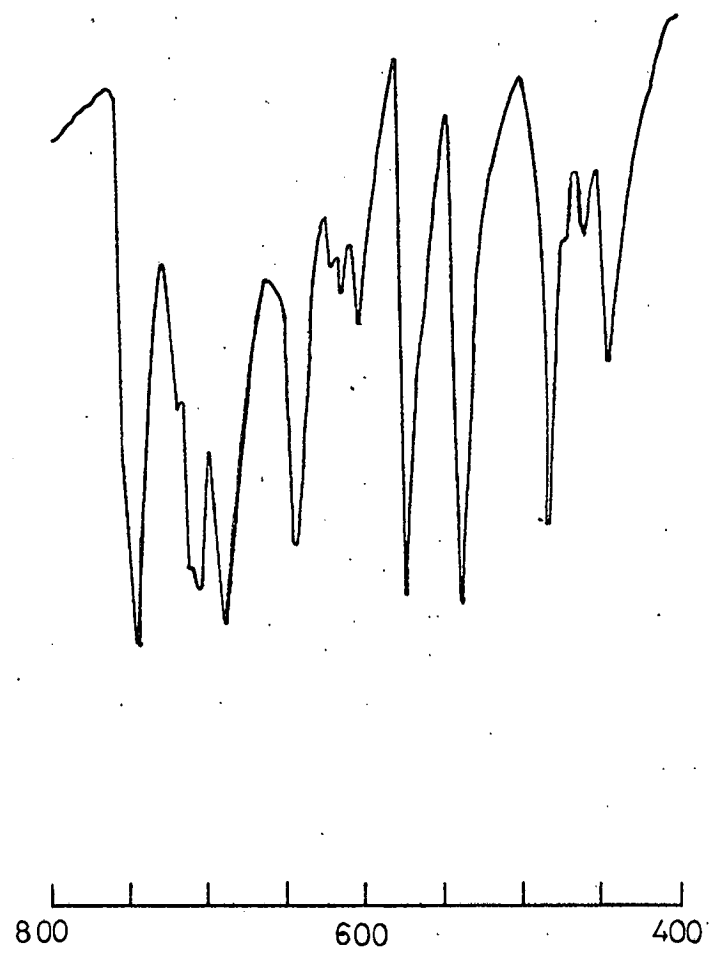
pale yellow form
(nujol mull)

solution spectrum
(in CS_2)

Figure 2.2

FIGURE 2.3

I.r. spectrum of $Pt(S_2PPh_2)_2PMe_2Ph$ (Nujol Mull) 800-400 cm^{-1}



expected shifts of uncoupled PS_2^- vibrations with changes in the mode of coordination. However, examination of the i.r. spectra of the platinum and palladium complexes suggested that the vibrations at ca 540s, 570s, 603w, 645m cm^{-1} were characteristic for the 1:1 complex. The vibrations at ca 570s and 603w cm^{-1} were also present in the starting material $M(S_2PPh_2)_2$ and were tentatively assigned to bidentate ligand vibrations.

The ^1H n.m.r. spectra of the complexes $M(S_2PPh_2)_2PR_3$ (M=Pd, Pt; PR_3=PMe_2Ph, PPh_2Me) in carbon disulphide or deuterochloroform (Table 2.1) showed a doublet in the methyl region near τ7.70 ($J_{P-H} \simeq$ 11.3 Hz) indicating phosphine coordination [56]. In the platinum complexes an additional pair of doublets due to ^{195}Pt were observed ($J_{Pt^{195}-H} \simeq$ 38Hz), which corresponded closely to values found in other tertiary phosphine coordinated complexes of platinum [50, 56], and confirmed the coordination of the phosphine to the platinum atom, rather than reaction with the dithio-ligand. The chemical shifts and coupling constants were also found to be very close to those reported for methyldiphenylphosphine complexes of other platinum dithioates [50, 51] suggesting that a similar structure existed for all these complexes. The phosphine doublet for $Pd(S_2PPh_2)_2PMe_2Ph$ in carbon disulphide was very broad suggesting considerable exchange between the coordinated phosphine and free phosphine occurred as a result of partial dissociation of the complex to $M(S_2PPh_2)_2$ and free phosphine. Similar exchange of the phosphine in related complexes has been reported by Fackler [51].

TABLE 2.1

^{1}H N.m.r. data for some platinum and palladium tertiaryphosphine complexes at 301 K in the phosphine methyl region.

Compound	Solvent	τ Value[a]	J(P-H)[b]	J(Pt-H)[b]
$Pt(S_2PPh_2)_2PMePh_2$	CS_2	7.69	11.4	38.0
$Pt(S_2PPh_2)_2PMePh_2$	$CDCl_3$	7.67	11.3	37.5
$Pt(S_2CNEt_2)_2PMePh_2$[c]	$CDCl_3$	7.72	10.0	38.0
$Pt(S_2COEt)_2PMePh_2$[c]	$CDCl_3$	7.80	11.0	41.0
$Pd(S_2PPh_2)_2PMePh_2$[d]	CS_2	7.68	11.2	-
$Pt(S_2PPh_2)_2PMe_2Ph$	CS_2	8.08	11.3	38.0
$[Pt(S_2PPh_2)(PMePh_2)_2]-S_2PPh_2$	$CDCl_3$	7.99	13.2	49.5
$[Pt(S_2PPh_2)(PMe_2Ph)_2]-S_2PPh_2$	$CDCl_3$	8.27	12.6	49.0
$[Pt(S_2PPh_2)(PMe_2Ph)_2]-BPh_4$	$CDCl_3$	8.66	10.0	39.0

[a] $\pm$ 0.01. [b] Multiplicity: three doublets except where stated otherwise, J(P-H) $\pm$ 0.2 Hz; J(Pt-H) $\pm$ 0.5 Hz. [c] From reference 50. [d] One doublet.

The reaction of $Pt(S_2PPh_2)_2$ with PPh_3 (1:1 molar ratios) was studied more thoroughly since temperature variable products were obtained for the analogous palladium complex[52]. At room temperature, the addition of light petroleum to the reaction mixture gave an initial pale flocculent precipitate which rapidly changed to a fine bright yellow precipitate of the type described earlier. However, precipitation at low temperature (ca 200 K) gave a pale yellow precipitate which remained stable at room temperature. Both analysed for $Pt(S_2PPh_2)_2PPh_3$ but had different melting points and mull i.r. spectra (Figures 2.2a and b). The solution i.r. spectra in benzene or carbon disulphide were identical (Figure 2.2c) and the compounds could readily be interconverted by dissolution and reprecipitation at the appropriate temperature. These observations were consistent with the formation of isomers. All the mull and solution i.r. spectra showed the characteristic bands at ca 540s, 570s, 645m cm^{-1} suggesting that the ligand coordination was unchanged. The differences in the spectra appeared to be associated with the phenyl vibrations of the ligand and tertiary phosphine (ca 700 and 500 cm^{-1}) and may possibly be explained by different orientations of the bulky PPh_3 ligand with respect to the $^-S_2PPh_2$ groups. The solution i.r. spectra in carbon disulphide were very similar to the mull spectrum of the low temperature form except for an additional weak band at ca 675 cm^{-1} whose intensity increased with concentration. This vibration was thought to be due to solvation of a common intermediate in solution of a similar structure

to that of the low temperature isomer. $Pd(S_2PPh_2)_2PPh_3$ was also found to exist as two isomers and showed very similar behaviour to the platinum isomers, except that interconversion between the two forms took place in the solid state [52]. This difference in behaviour between palladium and platinum can be attributed to the increased lability of palladium substitution reactions compared with those of platinum.

No evidence for isomer formation was obtained with other phosphines, possibly since the smaller tertiary phosphine groups were less likely to take up different orientations with respect to the S_2PPh_2 groups.

2.4 Reaction of $M(S_2PPh_2)_2$ with triphenyl-arsine and -stibine

Treatment of cis $PtCl_2(AsPh_3)_2$ with diphenylphosphinodithioic acid gave a mixture of $Pt(S_2PPh_2)_2$ and $Pt(S_2PPh_2)_2AsPh_3$. However, the reaction of $Pt(S_2PPh_2)_2$ in benzene suspension with a large excess of triphenylarsine (1:5 molar ratios) gave a bright yellow solution from which the bright yellow product $Pt(S_2PPh_2)_2AsPh_3$ was obtained. The corresponding triphenylstibine complex $Pt(S_2PPh_2)_2SbPh_3$ was obtained by reaction of $Pt(S_2PPh_2)_2$ with an even greater excess of triphenylstibine (1:20 molar ratios). The mull i.r. spectra of these complexes were identical to the bright yellow triphenylphosphine complex, apart from the differing ligand vibrations. The attempted isolation of pale yellow isomers, by cooling the solutions to 200 K was unsuccessful.

Unlike the tertiary phosphine complexes, the triphenylarsine

or stibine complexes were unstable in solution, and dissociation to $Pt(S_2PPh_2)_2$ and free ligand ($AsPh_3$ or $SbPh_3$) occurred slowly in the case of the arsine complex, and rapidly for the stibine complex. This was shown by the solution i.r. spectra in benzene, dichloromethane, and carbon disulphide, and by the attempted molecular weight determination in chloroform where values of ca half that calculated for the monomeric structure were found. In dichloromethane the complexes were non-conducting.

In contrast, no reaction was obtained under any conditions between $Pd(S_2PPh_2)_2$ and triphenylarsine or stibine, a fact which can probably be attributed to the formation of stronger Pd-S bonds compared with Pd-As or Pd-Sb bonds, although steric factors may also be of some importance.

2.5 Reaction of $M(S_2PPh_2)_2$ with other ligands.

Reaction of $Pt(S_2PPh_2)_2$ in benzene solution with triphenylphosphite, triethylphosphite, and tetracyanoethylene (1:1 molar ratios), and with an excess of pyridine, 2,2' bipyridyl, sym-diphenylacetylene, 1,10 phenanthroline or dimethylsulphide gave yellow solutions. The similarity of the i.r. solution spectra with that of the phosphine complexes (in the 600-400 cm^{-1} region) suggested that some formation of complexes of form $Pt(S_2PPh_2)_2L$ (L=ligand as above) with a similar structure to the tertiary phosphine 1:1 complexes had occurred. The products were, however, either not isolable, or were only obtained as sticky solids on solvent removal. No reaction occurred with dimethylsulphoxide, norbornadiene, or allyl chloride.

No evidence of reaction between $Pd(S_2PPh_2)_2$ and any of the above bases, except triphenylphosphite was observed [52].

2.6 Reaction of $M(S_2PPh_2)_2$ with an excess of tertiary phosphine

When a suspension of $Pt(S_2PPh_2)_2$ in benzene (or dichloromethane) was shaken with an excess of any tertiary phosphine, the initial yellow solution rapidly became colourless, and partial removal of the solvent under reduced pressure gave white powders of stoicheiometry $Pt(S_2PPh_2)_2(PR_3)_2$ (PR_3=PPh_3, PPh_2Me, PMe_2Ph). By comparison, [52] $Pd(S_2PPh_2)_2$ was found to form 1:2 adducts only with PEt_3, PMe_2Ph, PPh_2Me, and not with PPh_3 or $PEtPh_2$, which was attributed initially to steric hindrance effects around the slightly smaller palladium atom. The mull i.r. spectra of the palladium and platinum complexes were identical (apart from the varying phosphine vibrations) and differed from those of the 1:1 adducts, suggesting a different coordination of the ligand. From the i.r. spectra it appeared that the vibrations at ca 560s, 570s, 605w, 650m cm^{-1} were characteristic of the 1:2 complexes (Figures 2.4 and 2.5). The vibrations at ca 570, 605 cm^{-1} were also present in $M(S_2PPh_2)_2$ and $M(S_2PPh_2)_2PR_3$, but the vibrations at ca 560, 650 cm^{-1} were not found in either of these other compounds.

In non polar solvents, such as benzene (dielectric constant ε=2.28) and carbon disulphide ε = 2.64) the 1:2 adducts were unstable and readily dissociated to give the 1:1 complex and free tertiary phosphine. The process could be monitored by successive i.r. spectra, by observing the growth of the strong band characteristic

FIGURE 2.4

I.r. spectrum of $[Pt(S_2PPh_2)(PPh_3)_2]S_2PPh_2$ (Nujol Mull) 800-400 cm^{-1}

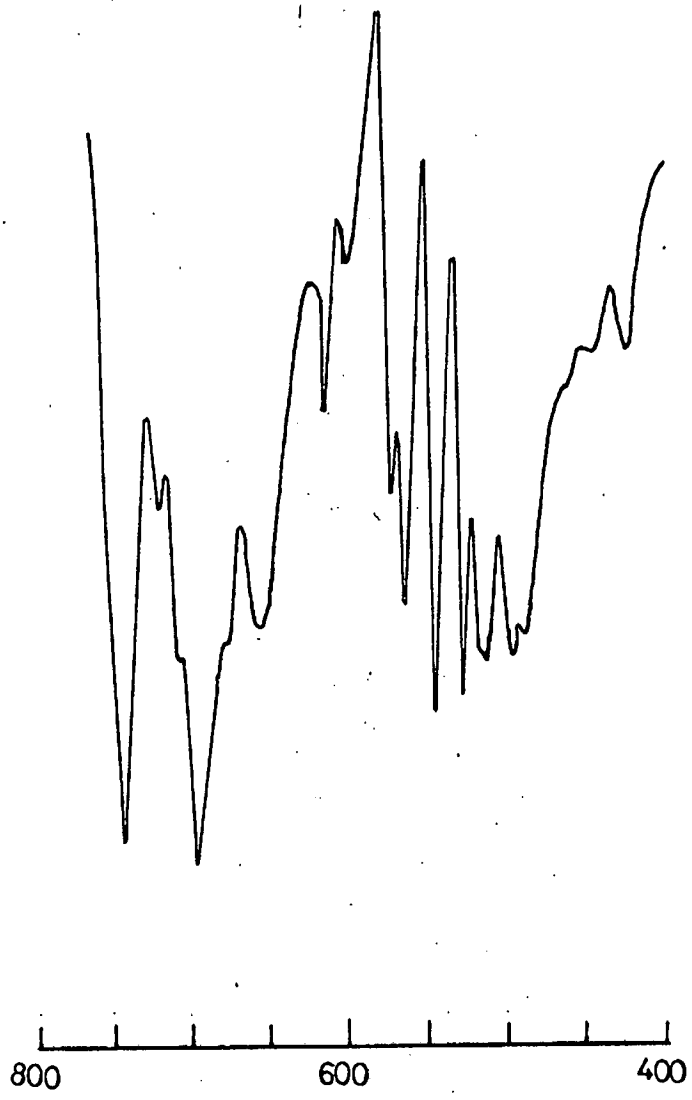
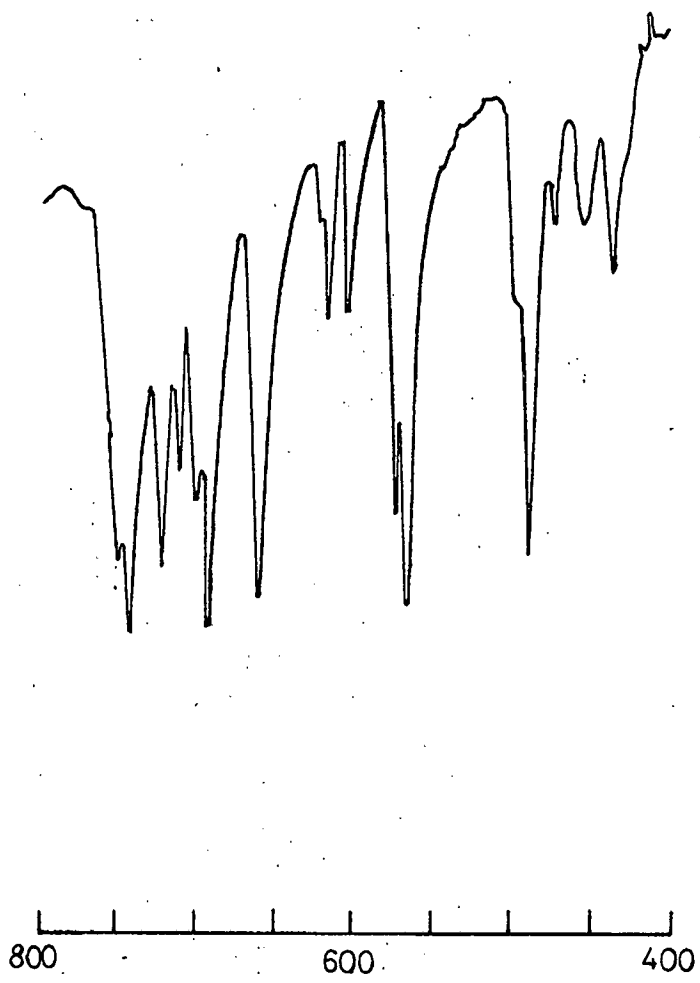


FIGURE 2.5

I.r. spectrum of $[Pt(S_2PPh_2)(PMe_2Ph)]S_2PPh_2$ (Nujol Mull) 800-400 cm^{-1}



of the 1:1 complexes (ca 540 cm^{-1}) and the loss of the one characteristic of the 1:2 species (ca 560 cm^{-1}). The addition of excess tertiary phosphine partially stabilised the 1:2 species in these solvents, as was also found for the palladium complexes [52]. The 1:2 complexes could also be partially stabilised by lowering the temperature of the solution.

However, in more polar solvents such as chloroform (ε=4.81), dichloromethane (ε =9.08) and in nitromethane (ε ca 28) the platinum 1:2 species were stabilised. No difference was observed between the mull i.r. and solution i.r. spectra (in the region 600-480 cm^{-1}) suggesting that little structural difference between the solution and solid state forms existed for these complexes.

Conductivity measurements in dichloromethane and nitromethane on the 1:2 complexes (and also on the 1:1 complexes with added phosphine) (Table 2.2) were consistent with their behaviour as 1:1 electrolytes. A molecular weight determination of $[Pt(S_2PPh_2)(PMe_2Ph)_2]S_2PPh_2$ in chloroform gave a value for the molecular weight which was half that expected, and this could be attributed to the dissociation of the complex into two ions. Conductivity measurements of the analogous palladium complexes (Table 2.2) confirmed that these complexes were also ionic. In nitromethane the complexes $[Pd(S_2PPh_2)(PR_3)_2]S_2PPh_2$ (PR_3=PMe_2Ph, PPh_2Me, PEt_3) were completely stabilised, but in less polar solvents such as dichloromethane and chloroform some breakdown of the complexes into the 1:1 species and free tertiary phosphine occurred, as shown

TABLE 2.2

Equivalent conductivities (298 K) of some platinum and palladium 1:1 and 1:2 diphenylphosphinodithioato-complexes.

Solvent	Compound	conc^{n} (10^{-4}M)	Λ^{a}	Λ^{a} plus excess of PR_3
CH_2Cl_2	$Ph_4AsCl.HCl$	9.8	55.3	-
	$Bu^{n}_4NClO_4$	10.1	22.7	-
		3.1	32.1	-
	$Pt(S_2PPh_2)_2$	8.8	0.09	-
	$Pt(S_2PPh_2)_2PPh_3$	9.4	0.72	32.3
	$Pt(S_2PPh_2)_2PMePh_2$	8.1	1.2	29.8
	$Pt(S_2PPh_2)_2PMe_2Ph$	12.1	0.63	23.0
	$Pt(S_2PPh_2)_2AsPh_3$	8.6	0.21	10.9[b]
	$[Pt(S_2PPh_2)(PPh_3)_2]S_2PPh_2$	8.8	26.6	-
	$[Pt(S_2PPh_2)(PMePh_2)_2]S_2PPh_2$	8.6	30.2	-
	$[Pt(S_2PPh_2)(PMe_2Ph)_2]S_2PPh_2$	12.0	33.2	-
	$[Pt(S_2PPh_2)(PMe_2Ph)_2]BPh_4$	9.2	33.6	-
	$[Pt(S_2PPh_2)(PMe_2Ph)_2]Cl$	8.4	41.9	-
	$[Pt(diphos)_2](S_2PPh_2)_2$	1.7	21.7	-
	$[Pt(diphos)_2](BPh_4)_2$	1.4	31.2	-
	$Pd(S_2PPh_2)_2PPh_3$	8.8	0.64	19.2
	$Pd(S_2PPh_2)_2PEtPh_2$	15.7	1.8	20.0
	$Pd(S_2PPh_2)_2PMe_2Ph$	13.7	2.5	26.4
	$Pd(S_2PPh_2)_2PMePh_2$	10.0	1.5	31.6
	$[Pd(S_2PPh_2)(PMe_2Ph)_2]S_2PPh_2$	12.0	24.4	-

/...

Table 2.2 continued.

Solvent	Compound	conc^{n} (10^{-4}M)	Λ^{a}	Λ^{a} plus excess of PR_3
	$[Pd(S_2PPh_2)(PMePh_2)_2]S_2PPh_2$	5.5	16.8	-
	$[Pd(S_2PPh_2)(PEt_3)_2]S_2PPh_2$	8.3	25.0	-
	$[Pd(diphos)_2](S_2PPh_2)_2$	4.1	36.8	-
CH_2Cl_2/ pyridine	$Ni(S_2PPh_2)_2(C_5H_5N)_2$	17.8	1.7	-
CH_3NO_2	$[Pt(diphos)_2](S_2PPh_2)_2$	1.4	66.6	-
	$[Pd(diphos)_2](S_2PPh_2)_2$	2.6	74.7	-
----	$[Pd(S_2PPh_2)(PMePh_2)_2]S_2PPh_2$	4.8	42.0	-
	$Pd(S_2PPh_2)_2PMePh_2$	11.4	8.3	53.0

a $cm^2 ohm^{-1} mole^{-1}$ b addition of excess $AsPh_3$

by the presence of a weak band at 540 cm^{-1} in the i.r. solution spectra. Clearly the conducting nature of the complexes in solution was incompatible with the non-ionic six-coordinate structure previously suggested [52].

Further confirmation of the ionic character of the 1:2 complexes was shown by ion exchange. The $^{-}S_2PPh_2$ anion in the complexes $[M(S_2PPh_2)(PR_3)_2]S_2PPh_2$ was readily replaced by chloride ion on treatment with Biorad chloride anion exchange resin, or by the tetraphenylborate ion by shaking with sodiumtetraphenylborate. The complexes obtained $[M(S_2PPh_2)(PR_3)_2]X$ (M=Pd, Pt; X=Cl, BPh_4) also showed conductivities in polar solvents typical for 1:1 electrolytes (Table 2.2). The i.r. spectra showed loss of the bands at ca 560 and 650 cm^{-1} suggesting that these vibrations were characteristic of the ionic diphenylphosphinodithioato-ligand vibrations. These vibrations are also present in the i.r. spectra of CsS_2PPh_2, xH_2O.

The reaction of $M(S_2PPh_2)_2$ (M=Pd, Pt) with excess of 1,2-bis(diphenylphosphino)ethane ($Ph_2PCH_2CH_2PPh_2$ [diphos]) produced white complexes of stiochelometry $M(S_2PPh_2)_2(diphos)_2$. Conductivity measurements indicated that the complexes could be formulated as $[M(diphos)_2]^{2+}(S_2PPh_2)_2^{2-}$. The i.r. spectra showed only the vibrations at ca 560, 650 cm^{-1} (with loss of the vibrations at ca 570 and 603 cm^{-1}) in agreement with the previous assignment for characteristic ionic $Ph_2PS_2^{-}$ vibrations. The $^{-}S_2PPh_2$ anion could be readily exchanged by the tetraphenylborate ion, producing $[M(diphos)_2](BPh_4)_2$ which showed none of the characteristic $Ph_2PS_2^{-}$

vibrations in the i.r. spectra.

The ^{1}H n.m.r. spectra of $[Pt(S_2PPh_2)(PR_3)_2]S_2PPh_2$ (PR_3= PMe_2Ph, PPh_2Me) (Table 2.1) in deuterochloroform showed three doublets near τ8.0 ($J_{P-H} \simeq 13$Hz, $J_{Pt-H} \simeq 49$Hz) confirming coordination of both the phosphines to platinum, and strongly suggesting a cis arrangement of the phosphines ($J_{P-P} \simeq 0$ Hz). A trans arrangement of the phosphines would be expected to exhibit 'virtual coupling' ($J_{P-P} \gg 0$) producing an apparent 1:2:1 'triplet' with J_{P-H} 5 Hz[56]. However, recent ^{1}H n.m.r. studies of some trans phosphine square planar complexes have shown doublet, singlet or triplet resonances[57] so that the ^{1}H n.m.r. spectrum cannot be used as an absolute confirmation of the structure. The ^{1}H n.m.r. spectra of the analogous palladium complexes showed the expected broad resonances due to the mixture of free tertiary phosphine, 1:2 and 1:1 species present in solution which are undergoing rapid exchange at room temperature.

Although no evidence for the formation of $[Pt(S_2PPh_2)(AsPh_3)_2]$-S_2PPh_2 of $[Pd(S_2PPh_2)(PR_3)_2]S_2PPh_2$ (PR_3=PPh_3, PPh_2Et) in benzene was obtained in these and earlier studies[52], the addition of the appropriate tertiary phosphine or arsine to a solution of the 1:1 adduct in dichloromethane produced a lightening of the solution colour, and an increase of the conductivity. The low λ value (maximum value ca 11 at 0.001 M) obtained for the arsine complex with excess ligand suggested that only 30-40^o/o conversion to the ionic species occurred which was too small to show any change in the i.r.

solution spectra. The conductivity of the palladium 1:1 complexes (PR_3=PPh_3, PPh_2Et) with excess of the tertiary phosphine (Table 2.2), however, suggested an appreciable conversion to the ionic form, which was also shown by the presence of a weak band at ca 560 cm^{-1} in the solution i.r. spectrum. In all cases, however, attempts to isolate the ionic species with these phosphines or arsines proved unsuccessful.*

Attempts to coordinate a second less sterically crowded tertiary phosphine were made. For example, the addition of triethylphosphine to $Pd(S_2PPh_2)_2PPh_3$ or triphenylarsine to $Pt(S_2PPh_2)PPh_3$ produced a lightening of the solution colour indicating some reaction to form the ionic species, with probable formation of the mixed ligand species, but no products were isolable.**

2.7 Structures of the Complexes

The similarity of the i.r. spectra, conductivity measurements and ^1H n.m.r. spectra of the palladium (II) and platinum (II) diphenylphosphinodithioato-complexes indicated that both metals formed compounds of closely similar structures. The 1:1 and 1:2 palladium complexes were initially postulated by Stephenson et al. to have the five and six coordinate structures (1) and (2) respectively chiefly from an interpretation of their i.r. spectra[52].

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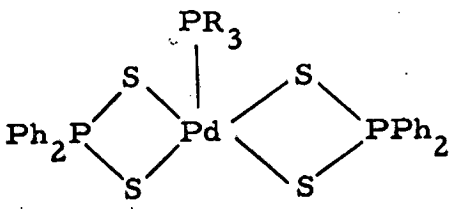
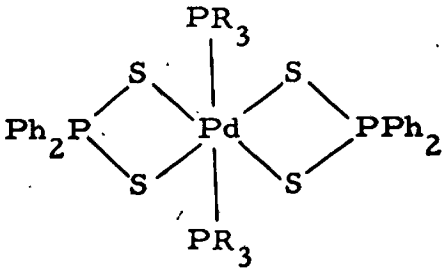
* However more recent work (D.F. Steele and T.A. Stephenson J. Chem. Soc. (Dalton) (1974) 2124) has shown that the $[Pd(S_2PPh_2)(PPh_3)_2]^+$ cation can be isolated from methanolic solution by addition of either $NaBPh_4$ or NH_4PF_6.

** Further work (M.C. Cornock and T.A. Stephenson - unpublished work) reveals that these mixed ligand complexes can be isolated as their BPh_4^- salts.



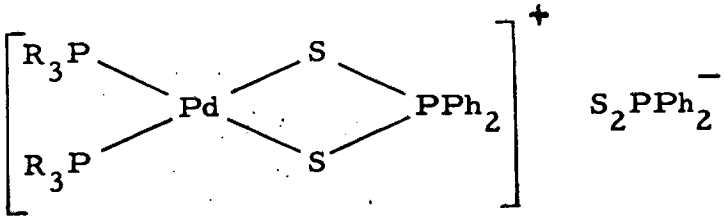
(1)



(2)

This type of adduct formation (without cleavage of the chelate ring) had already been shown to be common in the reactions of the nickel dithio-complexes with amines. The trans octahedral structure for the bis-adducts of nickel had been confirmed by the X-ray studies of several bis-pyridine adducts [45,46], and the mono-adduct [Ni(S_2PEt_2)$_2$-Quinoline] had been shown to have a square pyramidal structure [48], similar to those shown in (2) and (1) respectively. Although five and six coordination is rare for palladium and platinum, it is not unknown (see Chapter 1 [9-20]). Furthermore, Fackler's interpretation of the ^{1}H n.m.r. spectra of methyldiphenylphosphine complexes with other palladium (II) and platinum (II) dithioates strongly supported the formation of five and six coordinate complexes [40, 50, 51].

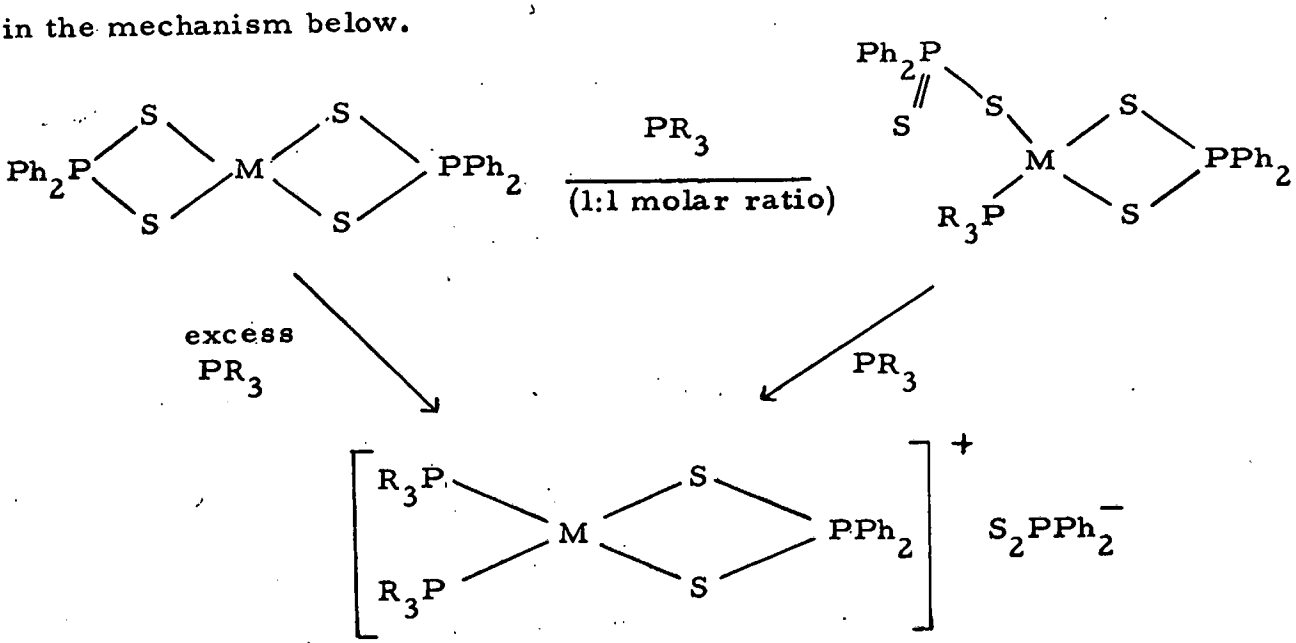
However, the conducting nature of the complexes [M(S_2PPh_2)$_2$(PR_3)$_2$] in polar solvents, together with the evidence from ion exchange experiments and i.r. spectra proved incompatible with a non-ionic six coordinate structure. These complexes were therefore reformulated as four-coordinate compounds as shown in (3)



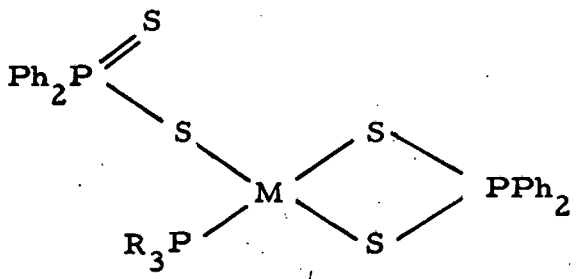
(3)

The crystal structure of $[Pd(S_2PPh_2)(PEt_3)_2]S_2PPh_2$ [58] confirmed the square planar coordination of palladium in the cation by two cis phosphines and a bidentate S_2PPh_2 ligand with $^-S_2PPh_2$ as the counter ion. The distances of the sulphur and phosphorus of the ion were 6.15 Å and 7.2 Å respectively from the palladium atom. The similarity of the solution and mull i.r. spectra of the 1:2 complexes indicated that the structure was essentially unchanged in solution.

Since the addition of tertiary phosphine occurred in a stepwise fashion, it appeared unlikely that the ionic complexes were obtained by addition of tertiary phosphine to a five coordinate 1:1 adduct $M(S_2PPh_2)_2PR_3$ (1) but rather that the addition of tertiary phosphine to the square planar chelate $M(S_2PPh_2)_2$ produced stepwise cleavage of one of the chelate rings, maintaining approximately square planar four coordination about the metal atom in all the complexes, as shown in the mechanism below.



The 1:1 complexes $M(S_2PPh_2)_2PR_3$ were therefore reformulated as four coordinate structures (4).

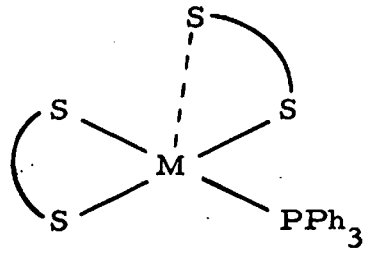


(4)

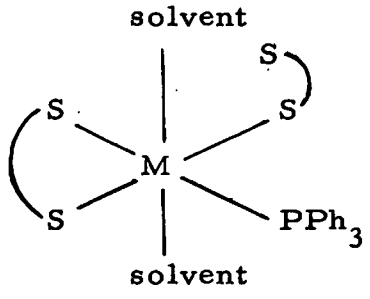
The crystal structure of $Pd(S_2PPh_2)_2PPh_3$ (for details see Chapter 3) confirmed the approximate square planar coordination about the palladium atom by the tertiary phosphine, a bidentate and a unidentate $^-S_2PPh_2$ ligand. The uncoordinated sulphur atom is 3.29 A^o above the square plane of the PdS_3P atoms (5).

The isolation of isomers for this PPh_3 complex and for the analogous platinum complex (see section 2.3) which showed closely similar i.r. mull and solution spectra in the region associated with the mode of bonding of the $^-S_2PPh_2$ group (ca 540, 570, 603, 645 cm^{-1}) suggested that the ligand coordination was essentially unchanged in all these forms. The changes in the region of the phenyl vibrations were consistent with different orientations of the unidentate $Ph_2PS_2^-$ ligand with respect to the bulky PPh_3 group. The i.r. spectrum showed evidence for a solvated species in solution, but apart from

this the i.r. mull spectrum of the low temperature species and the solution spectrum were virtually identical. A possible structure for the solution species is (6) in which the uncoordinated sulphur atom is in the same plane as the MS_3P atoms. This structure allows maximum interaction of the solvent with the complex, and the orientation of the uncoordinated sulphur atom enables the observed facile unidentate/bidentate exchange (presumably via cleavage of the M-S bond trans to the phosphine) to occur.



(5)



(6)

Removal of the solvent at low temperature gives the low temperature isomer which may have a similar structure to (6) (without solvent) which then rapidly reverts (for palladium) to give the thermodynamically more stable form (5). Unfortunately, the low temperature isomers were insufficiently crystalline for the X-ray confirmation of the structure.

The characteristic $Ph_2PS_2^-$ vibrations in the i.r. spectra for $M(S_2PPh_2)_2$, $M(S_2PPh_2)_2PR_3$, $[M(S_2PPh_2)(PR_3)_2]S_2PPh_2$ and related complexes can now be rationalised as vibrations due to the bidentate diphenylphosphinodithioato-ligand (ca 570, 603 cm^{-1}) , the unidentate ligand (ca 540, 645 cm^{-1}) and the ionic ligand (ca 560, 650 cm^{-1}) respectively as shown in Table 2.3. Although these bands can no longer

TABLE 2.3

Characteristic i.r. bands (700-500 cm^{-1}) of some diphenylphosphino-dithioato-complexes of palladium (II) and platinum (II).

Compound	Unidentate	Bidentate	Ionic
Ph_2PS_2H	638, 540	-	-
$Pt(S_2PPh_2)_2$	-	601, 567	-
CsS_2PPh_2	-	-	654, 562
$Pt(Pd)(S_2PPh_2)_2PMe_2Ph$	645, 539	603, 571	-
$Pt(S_2PPh_2)_2AsPh_3$	645, 539	603, 571	-
$Pt(S_2PPh_2)_2SbPh_3$	643, 539	603, 572	-
$Pt(S_2PPh_2)_2PPh_3$ [a]	645, 539	603, 571	-
$Pt(S_2PPh_2)_2PPh_3$ [b]	648, 540	603, 570	
$[Pd(S_2PPh_2)(PEt_3)_2]S_2PPh_2$	-	605, 573	650, 560
$[Pt(Pd)(S_2PPh_2)(PMePh_2)_2]S_2PPh_2$	-	603, 571	655, 562
$[Pt(Pd)(S_2PPh_2)(PMe_2Ph)_2]S_2PPh_2$	-	603, 570	656, 562
$[Pt(S_2PPh_2)(PMe_2Ph)_2]BPh_4$	-	603, 573	
$[Pt(S_2PPh_2)(PMe_2Ph)_2]Cl$	-	603, 573	
$[Pt(Pd)(diphos)_2](S_2PPh_2)_2$	-	-	650, 563
$[Pt(diphos)_2](BPh_4)_2$	-	-	-

[a] Bright yellow form. [b] Pale yellow form.

be assigned to specific vibrations, it is likely that these may contain an appreciable contribution from PS_2^- stretching vibrations. In the i.r. spectrum of $Ni(S_2PPh_2)_2py_2$ (recently shown to have a trans octahedral structure[46]) the bidentate vibrations are found at 632 cm^{-1} and 570 cm^{-1}. Similarly, studies on the diphenylphosphinodithioato-complexes of rhodium, ruthenium and osmium[59] indicate some variation in the higher energy band positions compared with those given in Table 2.3, although the lower energy band positions are very similar to those shown in the Table. By analogy with carboxylate complexes, where ν_1 is much more sensitive to changes in the metal than ν_2, this might suggest that the higher energy band possesses appreciable ν_1 character and the lower band ν_2 character.

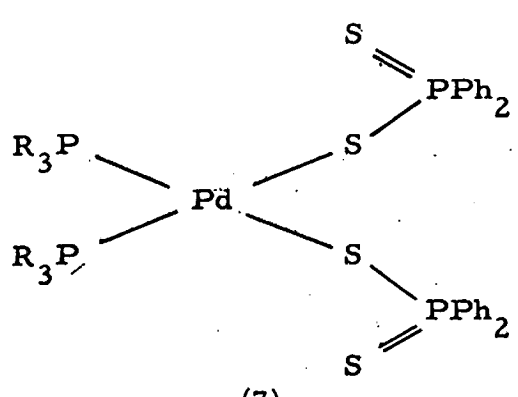
Similar reaction mechanisms have also been postulated by Tebbe and Muetterties[60] for the tertiary phosphine complexes of bis(difluorophosphinodithioato)palladium (II) from studies of the i.r. spectra and ^{19}F n.m.r. spectra, and more recent work on the tertiary phosphine (or arsine) complexes of dialkylphosphinodithioates (S_2PR_2; R=Me, Et[61]) has shown similar results, suggesting that the reaction mechanism postulated is general for all reactions of platinum and palladium phosphinodithioates with tertiary phosphines.

2.8 Reaction of $M(S_2PPh_2)_2$ with bulkier tertiary phosphines

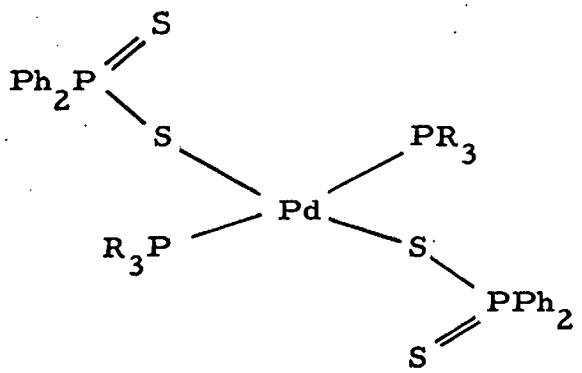
Preliminary studies of the reactions of $M(S_2PPh_2)_2$ (M=Pd, Pt) with the sterically bulkier tertiary phosphines $P(n\text{-}Bu)_3$ and $P(n\text{-octyl})_3$ were made. Solution i.r. studies with 1:1 molar ratios indicated the

expected formation of the complexes $M(S_2PPh_2)_2PR_3$ although solid products were only obtained for the palladium.

When $Pd(S_2PPh_2)_2$ was treated with an excess of these tertiary phosphines in benzene, yellow solutions were produced. Removal of the solvent gave yellow oils which on dissolution in diethyl ether and evaporation under a stream of nitrogen gave lemon-yellow solids. However, the mull i.r. spectra of the product obtained with $P(n\text{-}Bu)_3$ showed no vibrations at ca 603, 570 and 560 cm^{-1}, but showed a very strong band at ca 534 cm^{-1}, and similarly, that of the product obtained with $P(n\text{-octyl})_3$ showed a strong vibration at 535 cm^{-1} (together with a fairly strong band at 656 cm^{-1} and weak vibrations at 575, 565 cm^{-1}). When these complexes were dissolved in dichloromethane, the solution i.r. spectra and conductivities were typical of those found for the ionic species $[M(S_2PPh_2)(PR_3)_2]S_2PPh_2$ although these were not isolable. These observations were consistent with the initial formation of a cis or trans non-ionic species of stoicheiometry $M(S_2PPh_2)_2(PR_3)_2$ [(7) and (8) respectively] from the reaction in benzene, which on dissolution in the more polar solvent dichloromethane rearranged to the more usual ionic form (3).



(7)



(8)

It therefore appears possible that the reaction products may be influenced both by the nature of the solvent as well as by the tertiary phosphine size, but further studies are needed. The structure (8) is analogous to that postulated in the reactions of excess tertiary phosphine with palladium and platinum acetates in benzene[62]. More recent studies of the ^{1}H n.m.r. spectra, however, have shown a cis configuration for $Pd(OCOMe)_2(PPh_2Me)_2$ as in (7)[63a]. Preliminary studies of these reactions in more polar solvents have indicated the formation of ionic acetate complexes[63b] which are probably of a similar form to those obtained with the diphenylphosphinodithioato-ligand (3).

2.9 Experimental

Microanalyses were by the Analytical Laboratory, Edinburgh University and by A. Bernhardt, West Germany and are given in Table 2.4. Molecular weights were determined in dry ethanol-free chloroform at 37°C on a Mechrolab Osmometer (model 301 A), calibrated with benzil. I.r. spectra were recorded in the region 4000-250 cm^{-1} on a Perkin-Elmer model 457 and 225 Spectrometer using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. Spectra are listed for each compound (800-250 cm^{-1}). Conductivity measurements were made on a model 310 Portland Electronics conductivity bridge. N.m.r. spectra were obtained on a Perkin-Elmer model R10 60 MHz spectrometer and a Varian Associates HA 100 spectrometer. Mass spectra were measured on an AEI MS9 spectrometer, m.p.s were determined on a Kofler hot-stage microscope and are uncorrected.

Materials - Palladium (II) chloride and potassium tetrachloroplatinate (II)

(Johnson-Matthey); triphenylphosphine and dimethylphenylphosphine (B.D.H.), triphenylarsine (Emanuel), triphenylstibine (Koch-Light), triethylphosphine (B. Newton Main); ethyldiphenylphosphine and methyldiphenylphosphine were prepared by the Grignard method. Diphenylphosphinodithioic acid [64] and its caesium salt [52] were prepared as described previously.

Platinum compounds

Bis(diphenylphosphinodithioate)platinum (II):- Potassium tetrachloroplatinate (II) (1.81 g, 4.4 mmol) in a minimum volume of hot water (30 ml) was shaken for 72h with an excess of diphenylphosphinodithioic acid (5.70 g, 22.8 mmol) in ethanol (30 ml) to give a pale orange precipitate. After washing with water and ethanol, this was recrystallised from hot benzene (or dichloromethane) giving bright orange crystals of the complex which were washed with diethylether and dried *in vacuo* (2.5 g, 84 %). An alternative method of preparation is by reaction of platinum (II) acetate (prepared as in reference [62]) and excess diphenylphosphinodithioic acid in warm benzene to give an immediate orange precipitate, purified as above. A further method of synthesis from H_2PtCl_6 and Ph_2PS_2H has also been reported [54].

The compound is fairly soluble in dichloromethane, chloroform and hot benzene; sparingly soluble in acetone and ethanol; insoluble in water, ethers and hexane; ν max (Nujol) 745s, 718w, 709s, 685s, 619w,

601m, 567s, 485m, 463w, 454w, 360m, 296s.

Bis(diphenylphosphinodithioato)(triphenylphosphine)platinum (II):-

(a) Bright yellow form. $Pt(S_2PPh_2)_2$ (0.10 g, 0.15 mmol) was suspended in benzene (10 ml) and shaken with triphenylphosphine (0.04 g, 0.15 mmol) for ca 20 min. to give a lemon-yellow solution. Light petroleum (b.p. 100-120°) was then added to the solution giving a flocculent off-white precipitate which on trituration was rapidly converted into a crystalline bright yellow product. This was filtered off, washed with more petroleum (b.p. 60-80°), and dried in vacuo at 40° for several hours (0.12 g, 93%); νmax (Nujol) 755sh, 750sh, 742m, 706s, 693sh, 687s, 645m, 628w, 612w, 603w, 571s, 539s, 531s, 512m, 500w, 485w, 475w, 450w, 435w, 350m, 319w, 304w, 270w, 260w.

(b) Pale yellow form. A solution of the above product in carbon disulphide was cooled to ca 200 K and on addition of an excess of light petroleum (b.p. 100-120°) a pale yellow solid was obtained, washed with cold light petroleum (b.p. 60-80°) and air-dried; νmax (Nujol) 745s, 706s, 690s, 648s, 621w, 612w, 603w, 570s, 540s, 531s, 512m, 495w, 490sh, 465m, 365sh, 360m, 320w, 305w, 280w; νmax (CS_2, pale and bright yellow isomers) 742s, 706s, 690s, 675(variable), 648s, 623w, 612w, 603w, 570s, 540s, 530s, 512m, 495w, 490w.

Both the bright and the pale yellow compounds are soluble in dichloromethane and chloroform; sparingly soluble in carbon disulphide, benzene, and acetone and insoluble in ethanol and xylene. The complexes could also be obtained by treatment of

cis $Pt(PPh_3)_2Cl_2$ with HS_2PPh_2 under appropriate conditions.

Bis(diphenylphosphinodithioato)(triphenylarsine) platinum (II):- A suspension of $Pt(S_2PPh_2)_2$ (0.22 g, 0.31 mmol) in benzene (15 ml) was treated with an excess of triphenylarsine (0.5 g, 1.60 mmol) and shaken for 1h. Removal of the solvent under vacuum and treatment of the resulting oil with light petroleum(b.p.60-80°) gave a bright yellow precipitate which was washed carefully with light petroleum to remove free triphenylarsine and then dried in vacuo (0.29 g, 91°/o). Attempts to obtain a pale yellow isomer by cooling carbon disulphide or dichloromethane solutions of the above product were unsuccessful;

νmax (Nujol) 750s, 740s, 706s, 689s, 645s, 628w, 612w, 603w, 571s, 539s, 485w, 475m, 468m, 445w, 440sh, 360sh, 342m, 335m, 330m, 315w, 305m, 275w.

Bis(diphenylphosphinodithioato)triphenylstibine platinum (II):- As above, shaking $Pt(S_2PPh_2)_2$ (0.22 g, 0.31 mmol) and a large excess of triphenylstibine (2.0 g, 5.7 mmol) in benzene. Solvent removal under vacuum and treatment with dichloromethane and ethanol gave the product as a bright yellow powder. Excess of triphenylstibine was removed by repeated washing with light petroleum (b.p.60-80°) (0.18 g, 55 °/o);

ν max (Nujol) 749w, 730s, 706s, 687s, 643m, 626w, 612w, 603w, 572s, 539s, 483m, 472m, 445m, 365w, 350m, 312w, 305w, 290w, 273s, 265s.

Bis(diphenylphosphinodithioato)(dimethylphenylphosphine)-platinum (II):- A suspension of $Pt(S_2PPh_2)_2$ (0.23 g, 0.32 mmol) was shaken in

benzene (20 ml) with dimethylphenylphosphine (0.05 ml, 0.30 mmol) under nitrogen for 2h. After removal of any unreacted $Pt(S_2PPh_2)_2$, solvent was removed under vacuum and the residue treated with light petroleum (b.p. 40-60°) to give a pale yellow product (0.26 g, 95%)

ν max (Nujol) 745s, 718w, 712s, 709s, 690s, 645m, 623w, 615w, 603w, 571s, 539s, 483s, 471sh, 460w, 443m, 368m, 360m, 325w, 305w, 285w, 265w.

Bis(diphenylphosphinodithioato)methyldiphenylphosphine-platinum (II)

Method as above, $Pt(S_2PPh_2)_2$ (0.24 g, 0.32 mmol) and methyldiphenylphosphine (0.07 ml, 0.30 mmol) gave a pale yellow product (0.31 g, 98%):

ν max (Nujol) 740s, 720m, 709s, 690s, 645m, 621w, 612w, 603w, 571s, 541s, 510s, 488m, 455m, 430w, 365w, 360m, 312w, 305sh, 260w.

Attempts to prepare the complexes $Pt(S_2PPh_2)_2PR_3$ (PR_3 = $P(n\text{-}Bu)_3$ and $P(n\text{-octyl})_3$) by the method above or by the method used for the corresponding palladium complexes were unsuccessful and gave only sticky impure products.

(Diphenylphosphinodithioato)bis(triphenylphosphine)-platinum (II) Diphenylphosphinodithioate. $Pt(S_2PPh_2)_2$ (0.11 g, 0.16 mmol) in dichloromethane or benzene (20 ml) on shaking for 15 mins. with excess triphenylphosphine (0.20 g, 0.75 mmol) gave a colourless solution. Removal of the solvent under vacuum gave a semi-crystalline mass which on trituration with light petroleum (b.p. 40-60°C) gave an off-white powder (0.09 g, 55%). The compound is soluble in dichloromethane and chloroform; largely dissociated to $Pt(S_2PPh_2)_2$-PPh_3 in benzene, carbondisulphide, and insoluble in light petroleum.

ν max (Nujol) 743s, 720w, 710sh, 695s, 655m, 615w, 603w, 573s, 563s, 545s, 528s, 513s, 497s, 487s, 445w, 423w, 361m, 310m, 290w, 275w.

(Diphenylphosphinodithioato)bis(dimethylphenylphosphine)platinum (II) Diphenylphosphinodithioate. Method as above, except under nitrogen, $Pt(S_2PPh_2)_2$ (0.23 g, 0.32 mmol) and excess dimethylphenylphosphine (0.12 ml, 0.70 mmol) gave a white powder.

ν max (Nujol) 745s, 720m, 710m, 698sh, 690s, 656s, 615w, 603w, 570s, 562s, 495sh, 485s, 470w, 450w, 432m, 365m, 312w, 305w.

(Diphenylphosphinodithioato)bis(methyldiphenylphosphine)-platinum (II) Diphenylphosphinodithioate. Method as above, $Pt(S_2PPh_2)_2$ (0.18 g, 0.25 mmol) and excess methyldiphenylphosphine (0.20 ml, 0.85 mmol) in dichloromethane gave a white powder (0.22 g, 78%);

ν max (Nujol) 740s, 720m, 710m, 690s, 655m, 615w, 603w, 571s, 562s, 521m, 509m, 487m, 450m, 430w, 365m, 310w.

(Diphenylphosphinodithioato)bis(dimethylphenylphosphine)-platinum (II) Tetraphenylborate. $[Pt(S_2PPh_2)(PMe_2Ph)_2]S_2PPh_2$ (0.10 g, 1.1 mmol) in a minimum volume of acetone (3 ml) was treated with a concentrated aqueous solution of sodiumtetraphenylborate (1.0 g, 3.3 mmol). The immediate white precipitate was filtered off, washed thoroughly with distilled water, and then recrystallised from dichloromethane-light petroleum (b.p. 60-80°C) as a white powder.

ν max (Nujol) 790m, 755w, 745s, 740s, 730s, 720s, 709s, 690sh, 685m, 625w, 615w, 603m, 573s, 490m, 480m, 450w, 435w, 370m, 310m, 290w.

(Diphenylphosphinodithioato)bis(dimethylphenylphosphine)-platinum (II) Chloride. $[Pt(S_2PPh_2)(PMe_2Ph)_2]S_2PPh_2$ was shaken in dichloromethane

with an excess of Biorad chloride exchange resin (AG-1-X10; 200-400 mesh; Cl^- form) for several hours. Filtration, removal of the solvent, and trituration with light petroleum (b.p. 60-80°) gave a white powder; νmax (Nujol) 745s, 725s, 715s, 710s, 700s, 690s, 615w, 603w, 573s, 495m, 485m, 460m, 440w, 370m, 310m, 280w.

Bis [1, 2-bis(diphenylphosphino)ethane] platinum (II) Bis(diphenylphosphinodithioate). $Pt(S_2PPh_2)_2$ (0.20 g, 0.30 mmol) suspended in benzene with an excess of 1, 2-bis(diphenylphosphino)ethane (1.0 g, 2.5 mmol) gave an immediate white precipitate.

νmax (Nujol) 743s, 725m, 709sh, 695s, 675w, 650s, 612w, 563s, 530s, 510m, 487m, 480sh, 470w, 450w, 400w, 350m.

Bis[1, 2-bis(diphenylphosphino)ethane] platinum II - Bis(tetraphenylborate). $[Pt(diphos)_2](S_2PPh_2)_2$ and an excess of sodium tetraphenylborate were shaken for 24h in water-acetone. The white residue was washed with water, acetone, and light petroleum (b.p. 60-80°) and dried in vacuo;

νmax (Nujol) 790s, 765w, 750m, 745m, 738m, 730m, 709s, 690m, 679w, 621w, 612s, 534s, 512m, 485sh, 480s, 440m, 340m.

Attempts to prepare the non-ionic species $Pt(S_2PPh_2)_2(PR_3)_2$ (PR_3= $P(n\text{-}Bu)_3$ or $P(n\text{-octyl})_3$, for method see the corresponding palladium complexes) gave only intractable oils.

Palladium Complexes

$Pd(S_2PPh_2)_2$, $Pd(S_2PPh_2)_2PR_3$ (PR_3=PPh_3, PMe_2Ph, $PEtPh_2$ and PEt_3)

and $[Pd(S_2PPh_2)(PR_3)_2]S_2PPh_2$ (PR_3 = PMe_2Ph or PEt_3) were prepared as described in reference 52.

Bis(diphenylphosphinodithioato)methyldiphenylphosphine-palladium (II) Method as for the corresponding platinum complex, $Pd(S_2PPh_2)_2$ (0.18g, 0.25 mmol) and methyldiphenylphosphine (0.07 ml, 0.30 mmol) gave an orange crystalline product (0.18 g, 80%); ν max (Nujol) identical to the platinum complex.

Bis(diphenylphosphinodithioato)tri n-butylphosphine-palladium (II) $Pd(S_2PPh_2)_2$ (0.15 g, 0.25 mmol) suspended in CH_2Cl_2 with $P(n\text{-}Bu)_3$ (0.05 ml, 0.25 mmol) gave an orange solution, which on dissolution in diethyl ether deposited orange crystals on standing (12 hours).

Attempted isolation of the $P(n\text{-octyl})_3$ complex by the same method gave an intractable oil.

(Diphenylphosphinodithioato)bis(methyldiphenylphosphine)-palladium (II) Diphenylphosphinodithioate. Method as for the corresponding platinum complex, gave a pale orange powder; ν max (Nujol) identical to the platinum complex.

Bis[1,2-bis(diphenylphosphino)ethane]palladium (II) - Bis(diphenyl-Phosphinodithioate). Method as for the corresponding platinum complex, gave an immediate white precipitate; ν max (Nujol) identical to the platinum complex.

Bis(diphenylphosphinodithioato)bis(tri n-butylphosphine)-palladium (II) $Pd(S_2PPh_2)_2$ in benzene suspension with an excess of tri n-butylphosphine gave a yellow solution. Removal of the solvent under vacuo gave a yellow oil which on dissolution in diethyl ether followed by

evaporation under a stream of nitrogen gave a yellow product.

Bis(diphenylphosphinodithioato)bis(tri n-octylphosphine)-palladium (II)

Method as above, $Pd(S_2PPh_2)_2$ with an excess of tri n-octylphosphine gave a yellow product.

Nickel Compounds

Bis(diphenylphosphinodithioato)nickel (II) was prepared as described in reference 65; ν max (Nujol) 740s, 709s, 685s, 619w, 601w, 573s, 485m, 463w, 454w, 342m.

Bis(diphenylphosphinodithioato)bis(pyridine)nickel (II).

$Ni(S_2PPh_2)_2$ was suspended in chloroform and an excess of dry pyridine added dropwise. Immediate reaction occurred giving a deep yellow-green solution which on standing for several minutes deposited the pale green crystalline product. This was filtered, washed well with diethyl ether, and air-dried;

ν max (Nujol) 760s, 750s, 745s, 720w, 705s, 700s, 690s, 645w, 632s, 612s, 570s, 488m, 480m, 460m, 450m, 366s, 308w.

TABLE 2.4

Analytical data for some diphenylphosphinodithioato-compounds

Compound	m.p. (°C)	Found (%) C	H	Others	Mol.wt.[a]	Required (%) C	H	Others	Mol.wt.
$Pt(S_2PPh_2)_2$	298-300	41.9	2.9	P,8.8;S,20.0		41.6	2.8	P,8.9;S,18.5	
$Pt(S_2PPh_2)_2PPh_3$[b]	60-80	53.0	3.8	P,9.7;S,13.5		52.8	3.7	P,9.7;S,13.4	
$Pt(S_2PPh_2)_2PPh_3$[c]	109-110	52.6	3.6			52.8	3.7		
$Pt(S_2PPh_2)_2AsPh_3$	166	50.7	3.5			50.5	3.5		
$Pt(S_2PPh_2)_2SbPh_3$	130-132	48.2	3.4			48.2	3.4		
$Pt(S_2PPh_2)_2PMe_2Ph$	156-158	46.3	3.7		790, 0.02gml^{-1} 953, 0.11gml^{-1}	46.2	3.7		831
$Pt(S_2PPh_2)_2PMePh_2$	206-209	49.9	3.9		767, 0.02gml^{-1} 964, 0.04gml^{-1}	49.7	3.7		893
$[Pt(S_2PPh_2)(PPh_3)_2]S_2PPh_2$	69-70	61.0	4.3	P,10.4;S,10.7		60.7	4.2	P,10.4;S,10.8	
$[Pt(S_2PPh_2)(PMe_2Ph)_2]S_2PPh_2$	110	49.5	4.4	P,11.4;S,12.8	577, 0.004gml^{-1} 430, 0.009gml^{-1}	49.5	4.3	P,12.7;S,13.2	485
$[Pt(S_2PPh_2)(PMePh_2)_2]S_2PPh_2$	62-64	54.6	3.9			54.9	4.2		
$[Pt(S_2PPh_2)(PMe_2Ph)_2]BPh_4$	161-165	60.5	5.0			60.1	5.0		

/...

Table 2.4 continued.

Compound	m.p. (°C)	Found (%) C	H	Others	Mol.wt.[a]	Required (%) C	H	Others	Mol.wt.
$[Pt(S_2PPh_2)(PMe_2Ph)_2]Cl$	180-183	44.2	4.2	Cl, 4.6		44.5	4.2	Cl, 4.7	
$[Pt(diphos)_2](S_2PPh_2)_2$	245-248[d]	60.6	4.6			61.2	4.6		
$[Pt(diphos)_2](BPh_4)_2$	251-253[d]	73.3	5.6			73.7	5.4		
$Pd(S_2PPh_2)_2PMePh_2$	191-193	55.2	4.2			55.2	4.1		
$Pd(S_2PPh_2)_2P(n\text{-}Bu)_3$	98-107	54.0	5.7			53.6	5.8		
$[Pd(S_2PPh_2)(PMePh_2)_2]S_2PPh_2$	66-69	59.5	4.5			59.7	4.6		
$[Pd(diphos)_2](S_2PPh_2)_2$	211-212	65.6	5.6	P, 12.7; S, 8.7		65.0	4.9	P, 13.3; S, 9.3	
$Ni(S_2PPh_2)_2(C_5H_5N)_2$	160[d]	57.4	4.2	N, 3.7		57.1	4.2	N, 3.8	

[a] Determined in chloroform

[b] Bright yellow, room-temperature isomer

[c] Pale yellow low-temperature isomer

[d] With decomposition

CHAPTER 3

Crystal structure of Bis(diphenylphosphinodithioato) triphenylphosphine-palladium(II)

CHAPTER 3

The Crystal Structure of bis(diphenylphosphinodithioato)triphenylphosphinepalladium (II).

Dark orange needle-shaped crystals of $Pd(S_2PPh_2)_2PPh_3$ prepared as in reference 52 and recrystallised from a nitromethane-ether mixture were kindly supplied by B.D. Faithful. The crystals were mounted along the needle axis, and all photographs were obtained using Ni-filtered Cu-Xradiation (λ = 1.5418 Å).

3.1 Cell Dimension Determination

Preliminary oscillation and zero-layer Weissenberg photographs indicated a triclinic crystal. From the oscillation photograph the dimension of the needle axis (a) was found to be 9.684 Å with a standard deviation of 0.017 Å. The zero-layer Weissenberg film showed four prominent rows, two of which were very nearly 90° apart, and were chosen as the b* and c* axes. A comparison of the zero- and first-layer Weissenberg films indicated the lattice was B-centred (absences for all reflections where h+l = odd). The reciprocal cell dimensions b* (0.0538 $Å^{-1}$) and c* (0.04516 $Å^{-1}$) were obtained from the axial rows on the zero-layer Weissenberg film. The reciprocal cell angles γ^*(87.50 $\pm$ 0.17°) and β^*(89.67 $\pm$ 0.17 °) were obtained from c-axis and b-axis precession photographs respectively. An obtuse direct cell angle α(90.58 $\pm$ 0.17°) was obtained from the dial angle between these two settings. The remaining direct and reciprocal cell dimensions were obtained by calculation (Table 3.1).

TABLE 3.1

Crystal data for $Pd(S_2PPh_2)_2PPh_3$

Crystal System	Triclinic
Space Group	$B\bar{1}$, Z=4
Cell Dimensions	a = 9.684(30)Å
	b = 18.592(30) Å
	c = 22.145(30) Å
	α = 90.576(60)°
	β = 90.305(60)°
	γ = 92.497(60)°
Cell Volume	3983.19 $Å^3$
Density	do = 1.43 g cm^{-3} (by flotation)
	dc = 1.45 g cm^{-3}
Linear Absorption Coefficient	μ = 70.79 cm^{-1}

The crystal density was found by flotation in a potassium iodide-water solution since the crystals were soluble to varying extents in all organic solvents. The observed density of 1.43 g cms^{-3} was consistent with that calculated for four molecules in the unit cell (1.45 g cms^{-3}), indicating space group $B\bar{1}$ (alternative setting of $P\bar{1}$, no. 2) for the cell.

3.2 Preliminary Structure Determination from Precession Data

In order to give a fairly rapid confirmation of the arrangement of the heavy atoms of the ligands around the palladium atom (which had been inferred from the spectral properties), limited precession data out to a 2θ value of 73° was collected. Different dial settings enabled the planes hkl ($h=0 \rightarrow \pm 6$, $k=0 \rightarrow \pm 12$, $l=0,1,2,3$); hkl ($h=0 \rightarrow \pm 6$, $k=0,1,2,3$, $l=0 \rightarrow \pm 14$); hk2k and $hk\bar{2}k$ ($h=0 \rightarrow \pm 6$, $k=0 \rightarrow \pm 6$) to be obtained, these four dial settings corresponding to the four prominent axial rows on the zero-layer Weissenberg. 816 independent reflections were estimated visually, and Lorentz and polarisation corrections were applied [66].

A Patterson vector map was used to determine the heavy atom position. The largest peak on the map was considered to contain the Pd-Pd vector through the centre of symmetry. The coordinates of this peak were obtained ($u, v, w = 2x, 2y, 2z$) where u, v, w are the peak coordinates in Patterson space and x, y, z are the atom position coordinates in the crystal cell.

The Pd atom was then used as the phasing model for the structure. The calculated R factor for the structure, with only the

Pd contribution was O.538. The position of five of the other heavy atoms (phosphorus or sulphur) was readily obtained from the difference Fourier map. Average scattering factors for these atoms were then used in a subsequent difference Fourier map, which enabled the sixth heavy atom position to be determined, and a distinction between the sulphur and phosphorus atoms to be made.

Full matrix least squares refinement of these positions reduced the R factor to O.32. Further difference Fourier maps indicated the phenyl rings in the expected positions. The R factor, when approximate carbon positions were included, was O.27, and already confirmed that the arrangement around the Pd was square planar, with a coordinated phosphine, one bidentate and one unidentate phosphinodithioato-ligand, as shown in Figure 3.3.

3.3 Three Dimensional Weissenberg Data

Further data was obtained from equi-inclination Weissenberg photographs of crystals mounted along the needle axis. A small needle shaped crystal (considered as a cylinder of radius O.OO7 cms) was used to obtain the planes hkl (h=O,1,2, k=O → ±21, l=O → ±24). For the remaining layers (h=3→ 8) another needle shaped crystal (treated as a cylinder of radius O.O15 cms) was used, giving a total of 263O independent reflections out to a 2θ value of 135^{o}. The intensity estimation of this data was made by a SAAB AFS MKS II automatic film scanner, linked to a PDP 8 computer. The data was then corrected for Lorentz and polarisation effects [67].

3.4 Accuracy of Scanned Intensities

a) SAAB Scanner details

A small section of the film (60 x 90μm) is illuminated at a time by a light beam of carefully controlled stability and cross section. The light flux is measured by means of a photomultiplier and converted to a D.C. voltage which is proportional to the film transmission where

$$\text{transmission} = \frac{\text{transmitted light flux}}{\text{incident light flux}}$$

The film is rotated and translated by means of a feeder mechanism so that it is scanned along parallel tracks of width 90μm. Pulse signals are produced at the start of each track, and at every coordinate unit (60μm) along the track. At each pulse signal along the track, a value of the transmission is obtained (as a D.C. voltage which is then amplified by an A-D converter) and can be referred to the film sheet coordinates.

b) General

Within the linear range, the integrated intensity of a diffracted beam is proportional to the integrated optical density of the spot on the film, where the optical density at any point is given by

$$\text{optical density} = \log_{10} \left(\frac{\text{background transmission}}{\text{transmission}} \right).$$

Thus both the transmission and the background transmission measurements are critical for an accurate determination of the spot intensity.

The background caused by general scattering of the X-ray

beam varies relatively slowly, and for Weissenberg films it can be considered to be fairly constant along a line parallel to the central line [68]. All the films were scanned along tracks parallel to this direction, and so a fairly constant track background could be assumed.

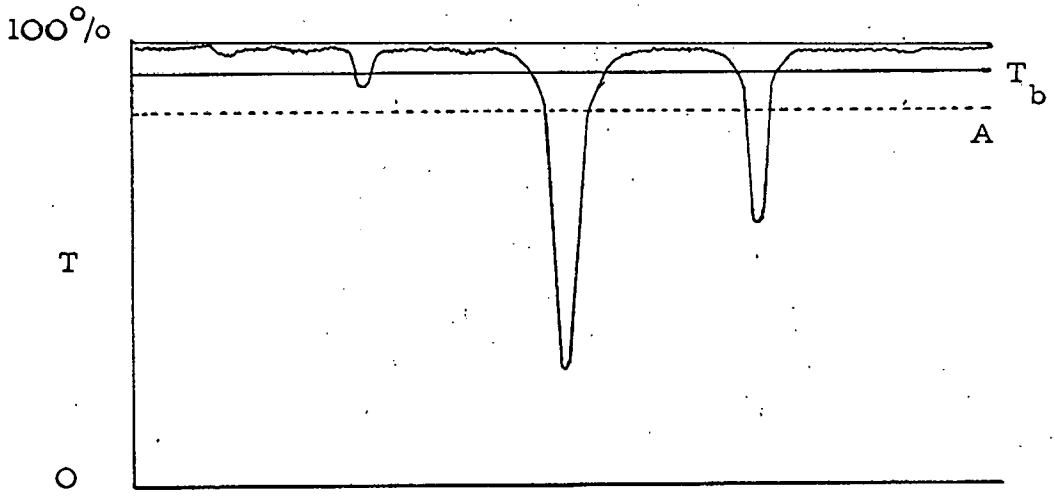
c) Errors introduced by the Data Collection

Due to the inadequate storage capacity of the PDP 8 computer, only a limited amount of the transmission data collected for each track could be kept. At the end of each track the mean transmission was calculated. Only a fraction of the transmission data below this mean value was stored. This fraction (usually 75-85^{o}/o depending on the film intensity) was set for each film at the start of the scan, and contained most (but not all) of the spot information (see Figure 3.1). The mean of the remaining transmission data was stored as the background transmission value. Although the background transmission is generally constant within a track (see above), the data used to calculate the track background transmission value included contributions from spots whose transmission was partly or wholly above the track mean transmission value (see Figure 3.1) and therefore gave an inaccurate value for the background transmission (and hence contributed to inaccuracy in the optical density). In addition, the lack of background measurements close to spots embedded in white radiation streaks made correction for the streak impossible.

d) Errors introduced by the Data Processing

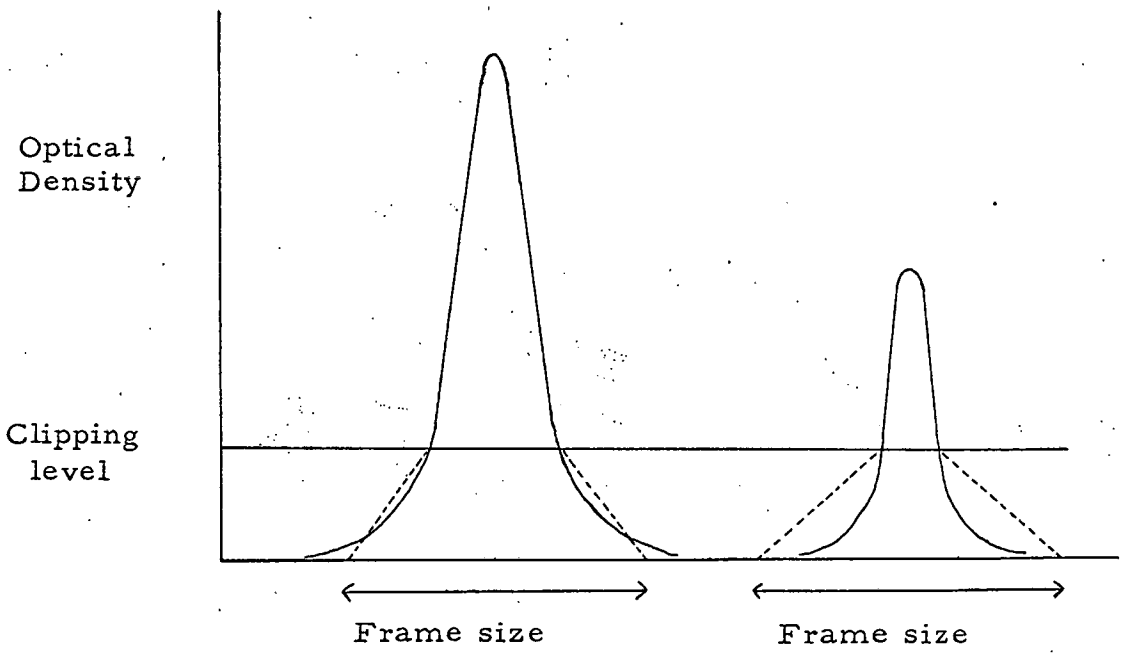
The initial processing of the scanner output involved a search

Figure 3.1



T = Transmission. Data above A not stored but used to calculate background transmission (T_b). Data below A stored.

Figure 3.2



to locate spots which existed as features in adjacent scanner tracks. The optical density (calculated for each point from the stored transmission data) was summed for the whole spot and referred to the film sheet coordinates which enabled the spot to be indexed.

In order to obtain the total optical density for each spot an estimate of the contribution from the region below the clipping level was made. Several assumptions were made in the program used. The spot shape and size were assumed to be constant throughout the film and were defined by a rectangular frame, and the density was assumed to fall linearly from the point at which it reached the clipping level to the edge of the frame (see Figure 3.2). Thus the contribution from this region could readily be calculated.

Even if the assumption about the fall in density was reasonable, considerable error was introduced by the assumption of constant spot size and shape. Since all the photographs of $Pd(S_2PPh_2)_2PPh_3$ were obtained using crystals with nearly cylindrical symmetry about the rotation axis, all the reflections on the zero-layer Weissenberg were of nearly the same size and shape. On the upper-layer Weissenberg films, however, the usual extension and contraction of spots close to the central line was found, with this effect increasingly marked on the highest levels. The use of a constant frame size to calculate the density contribution of the region below the clipping level would be expected to give an overestimate of the intensities of contracted spots. The program also tended to reject the extended spots on account of their shape.

The intensities of weak spots on all the films were also likely to be overestimated since these tended to be smaller in size than reflections of high intensity. This was a particular disadvantage since the Weissenberg films for $Pd(S_2PPh_2)_2PPh_3$ showed a wide variation of spot intensities, and the weak reflections contain contributions from the carbon atoms.

All the films showed reflections out to very high sin values where large splittings of the α_1, α_2 reflections were observed. These reflections were frequently rejected by the program on account of their shape, or missed completely since they lay too far from the position calculated by the program using the average Cu Kα-wavelength.

In addition, the Weissenberg photographs were obtained along only one axis of the triclinic system which meant that few reflections were estimated from more than one part of the film. Table 3.2 shows some analyses of the data by layers. The first of the columns shows the R factors obtained in the structure determination for spots close to the central line, where contraction or extension was observed, especially with increasing layer number. The next column shows the R factors for the middle part of both halves of the film where little expansion or contraction occurred and little or no α_1, α_2 splitting was observed, and the third column shows analyses of the high values where splitting was predominant. It can be seen that the R factors for the spots close to the centre are considerably poorer than the R factors for the middle area of the

TABLE 3.2

Analysis of the data obtained for $Pd(S_2PPh_2)_2PPh_3$

	LOW RANGE[a]		INTERMEDIATE[b]		HIGH RANGE[c]	
h[d]	n[e]	R[f]	n	R	n	R
0	23	21.9	81	12.7	157	11.8
1	48	20.4	134	11.7	247	9.2
2	36	18.8	142	11.0	240	9.2
3	33	12.8	91	10.7	100	15.1
4	30	19.4	127	10.0	156	14.8
5	38	18.2	123	9.6	200	13.8
6	25	25.9	123	13.1	165	11.9
7	25	10.9	51	11.8	36	16.8
8	11	10.3	55	16.5	22	23.6

[a] where $2k^2 + 31^2 \leqslant 108$. [b] where $108 < 2k^2 + 31^2 \leqslant 400$

[c] where $2k^2 + 31^2 > 400$

[d] h index. [e] Number of reflections. [f] R factor (x100)

film. Some particularly extended spots were of course excluded during the data processing stage, as were many of the split spots. Recent studies by Fraser on the accuracy of intensity values obtained by the same scanner processing, have also indicated the errors outlined above[58].

3.5 Refinement of the Structure

The heavy atom positions obtained from the previous precession data were used for a difference Fourier map, from which the approximate carbon atom positions were found. Least squares refinement of the heavy atom positions, including the carbon contribution gave the R factor as O.2O. The carbon atoms of each ring were then shifted to give an idealised phenyl ring in the best plane of the original atoms, and the plane described by three positional and three orientational parameters. These parameters, and the isotropic heavy atoms were refined by full matrix least squares. After correction of the data for absorption[69], the heavy atoms were refined anisotropically, reducing the R factor to O.158. Finally the ring size was varied improving the R factor slightly. A weighting factor w (w=1 for $Fo \leqslant A$, $w = \frac{A}{Fo}^2$ for $Fo > A$ where A=11O on the scale of Table 3.7) was used in the final refinement. All the atoms were then refined individually by full matrix least-squares to a final R factor of O.112.

The fractional coordinates and thermal parameters of each atom are listed in Table 3.3. A projection of the structure is shown in Figure 3.3 which also shows the labelling of all the atoms and

the thermal ellipsoids of the heavy atoms. Figure 3.4 shows a c-axis projection of the unit cell.

TABLE 3.3

Fractional coordinates of atoms and thermal parameters (x100) ($Å^2$)

	x	y	z	u
Pd	0.2261(2)	0.2562(1)	0.0570(1)	
S1	0.0900(8)	0.1762(4)	-0.0021(3)	
S2	0.1228(9)	0.3604(4)	0.0145(3)	
S3	0.3588(9)	0.3433(4)	0.1138(4)	
S4	0.3878(10)	0.2155(4)	-0.0786(4)	
P1	0.2125(8)	0.4094(3)	0.0855(3)	
P2	0.3236(7)	0.1701(3)	0.1134(3)	
P3	0.1899(8)	0.1875(4)	-0.0829(3)	
		Phenyl carbon atoms		
C1	0.1599(30)	0.1008(13)	-0.1195(11)	2.1(6)
C2	0.1247(36)	0.1010(16)	-0.1840(14)	4.0(8)
C3	0.1042(41)	0.0244(18)	-0.2074(15)	4.8(9)
C4	0.1346(39)	-0.0333(18)	-0.1791(15)	4.7(9)
C5	0.1800(46)	-0.0266(21)	-0.1168(18)	6.1(11)
C6	0.1945(32)	0.0390(14)	-0.0884(12)	2.3(7)
C7	0.3168(29)	0.0754(13)	0.0897(11)	1.6(6)
C8	0.4351(35)	0.0381(15)	0.0792(13)	3.3(7)
C9	0.4296(37)	-0.0355(16)	0.0652(14)	3.9(8)
C10	0.2990(38)	-0.0693(17)	0.0558(14)	4.4(8)
C11	0.1827(39)	-0.0310(16)	0.0649(14)	4.3(8)
C12	0.1855(34)	0.0409(14)	0.0822(12)	2.8(7)

Table 3.3 page 2

	x	y	z	u
C13	0.2819(31)	0.4961(14)	0.0704(12)	2.3(6)
C14	0.1913(45)	0.5461(20)	0.0537(17)	6.2(10)
C15	0.2700(62)	0.6204(26)	0.0316(22)	9.1(15)
C16	0.3985(58)	0.6310(25)	0.0372(21)	7.5(13)
C17	0.4757(48)	0.5826(21)	0.0584(17)	6.6(11)
C18	0.4266(44)	0.5145(20)	0.0729(16)	5.9(10)
C19	0.0967(34)	0.2473(15)	-0.1252(13)	3.2(7)
C20	-0.0486(49)	0.2379(22)	-0.1312(18)	6.8(12)
C21	-0.1318(50)	0.2869(22)	-0.1610(18)	6.6(12)
C22	-0.0494(56)	0.3497(24)	-0.1834(20)	8.7(13)
C23	0.0777(80)	0.3588(34)	-0.1776(28)	10.1(21)
C24	0.1610(47)	0.3103(21)	-0.1515(17)	6.5(10)
C25	0.4985(29)	0.1939(13)	0.1255(11)	1.9(6)
C26	0.5660(37)	0.2097(16)	0.1780(14)	3.9(8)
C27	0.6997(49)	0.2329(22)	0.1845(18)	6.7(11)
C28	0.7952(46)	0.2380(20)	0.1350(17)	5.6(11)
C29	0.7309(40)	0.2213(18)	0.0737(15)	4.5(9)
C30	0.5869(33)	0.1973(15)	0.0722(15)	2.7(7)
C31	0.0889(43)	0.4222(18)	0.1468(16)	5.2(9)
C32	-0.0515(61)	0.4156(26)	0.1303(22)	9.2(16)
C33	-0.1515(76)	0.4254(32)	0.1910(28)	11.9(21)
C34	-0.0645(104)	0.4357(41)	0.2442(37)	14.3(28)
C35	0.0656(100)	0.4410(40)	0.2546(35)	15.1(27)

Table 3.3 page 3

	x	y	z	u
C36	0.1343(77)	0.4224(33)	0.2048(30)	11.8(20)
C37	0.2440(29)	0.1654(13)	0.1864(11)	1.8(6)
C38	0.2774(36)	0.1106(16)	0.2246(13)	3.6(8)
C39	0.2002(37)	0.0991(16)	0.2828(14)	4.2(8)
C40	0.1039(33)	0.1456(15)	0.2936(12)	3.1(7)
C41	0.0689(41)	0.2077(18)	0.2576(15)	4.8(9)
C42	0.1501(38)	0.2162(16)	0.2033(14)	3.7(8)

Anisotropic thermal parameters (x100)

	U11	U22	U33	U12	U13	U23
Pd	0.5(1)	1.1(1)	0.9(1)	0.0(1)	0.0(1)	-0.1(1)
S1	1.25(5)	2.7(4)	1.9(4)	-0.6(3)	0.1(3)	-0.2(3)
S2	4.5(6)	1.9(4)	4.3(5)	1.1(4)	3.3(4)	-0.7(3)
S3	3.4(6)	2.0(4)	5.2(6)	-0.3(3)	-2.4(5)	0.1(4)
S4	1.9(6)	4.3(5)	5.3(5)	-1.0(4)	0.2(4)	-1.5(4)
P1	3.1(5)	0.9(3)	3.4(4)	0.2(3)	0.4(4)	0.2(3)
P2	0.8(5)	2.0(4)	1.6(4)	0.6(3)	-0.2(3)	-0.8(3)
P3	1.1(5)	2.4(4)	1.9(4)	-0.6(3)	0.6(3)	-0.7(3)

Projection of the molecule $Pd(S_2PPh_2)_2PPh_3$

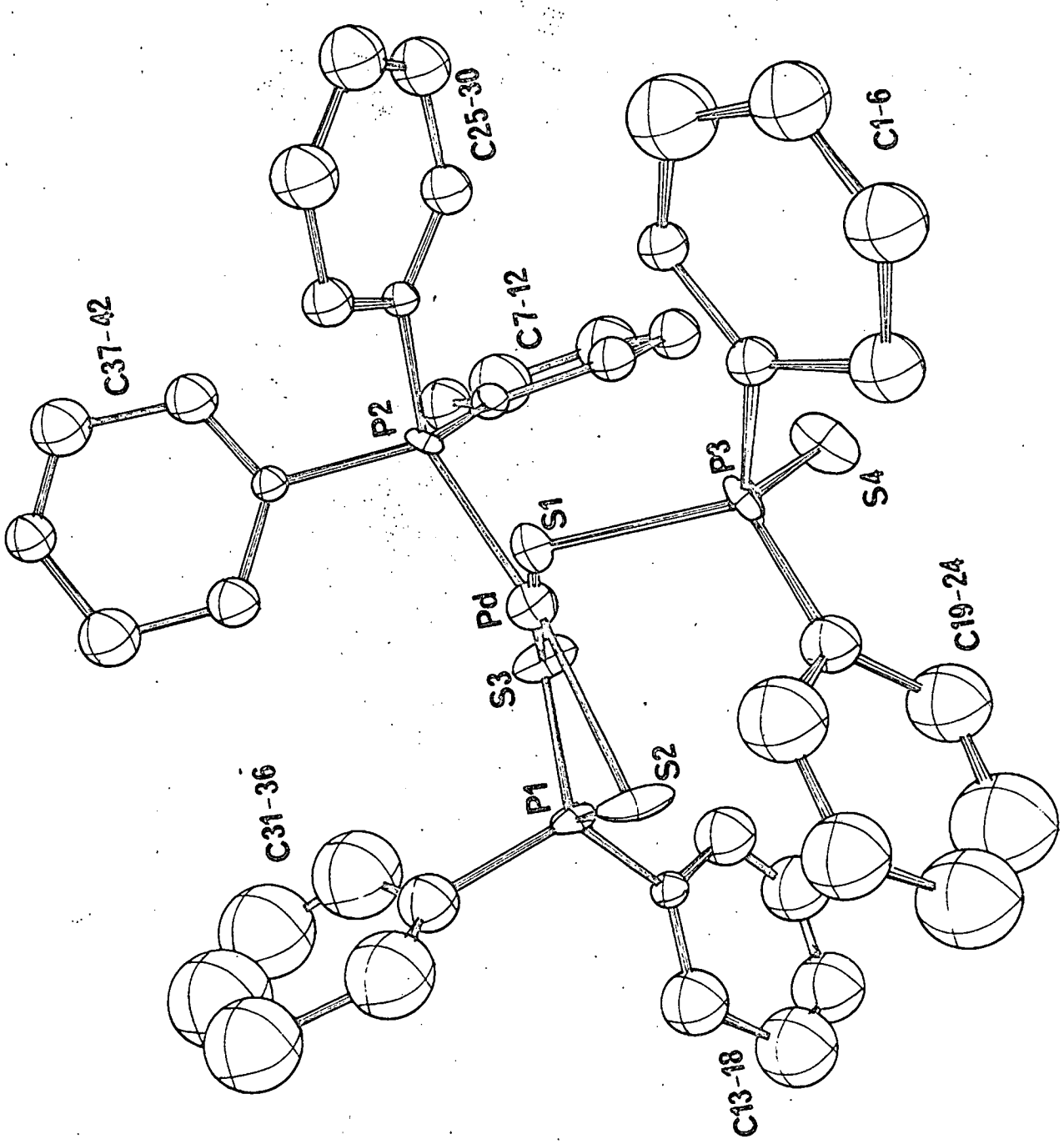


Figure 3.3

c-axis projection of the unit cell of $Pd(S_2PPh_2)_2PPh_3$

centred about the point $(\frac{1}{2}, \frac{1}{2}, 0)$

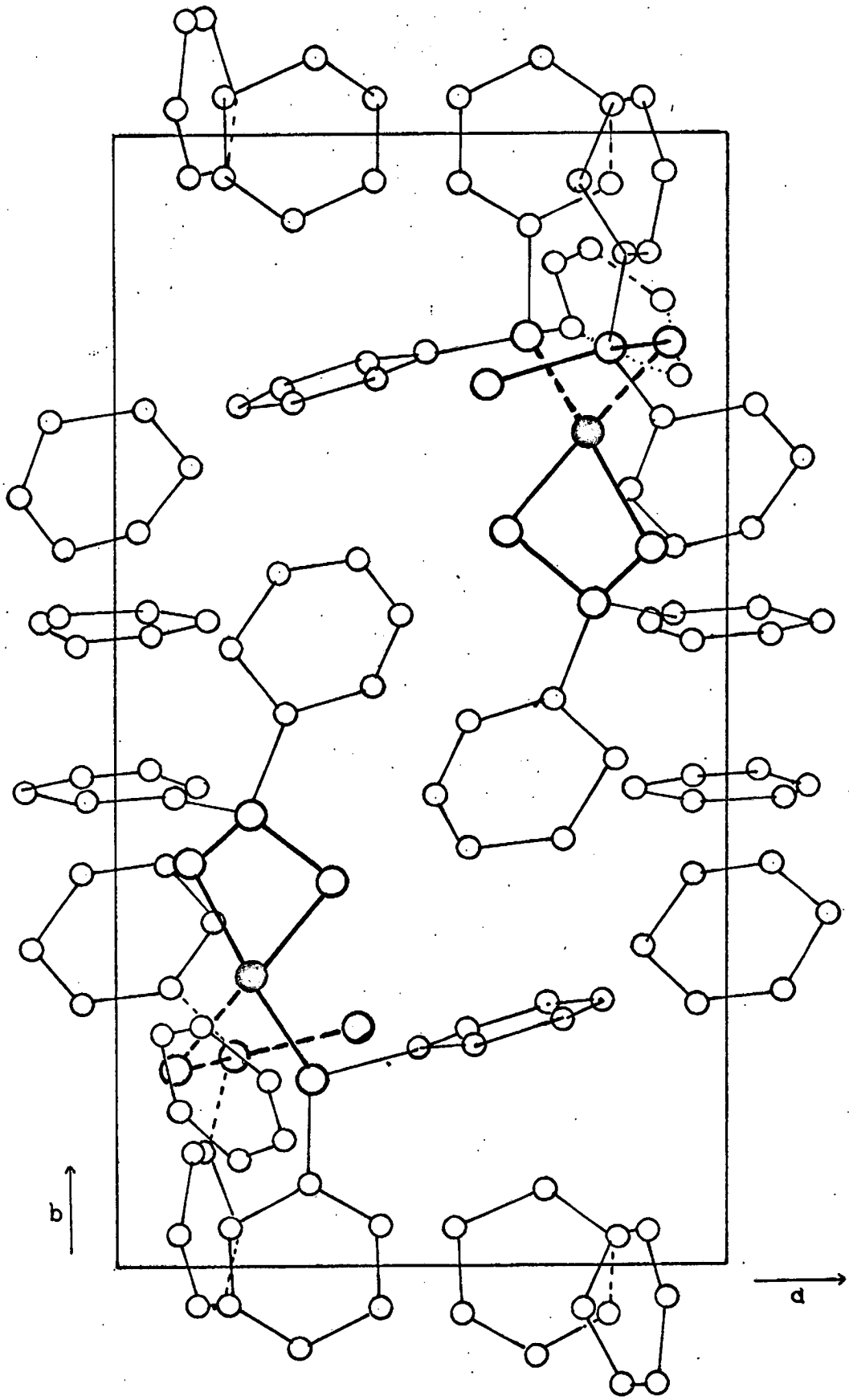


Figure 3.4a

c-axis projection of the unit cell of $Pd(S_2PPh_2)_2PPh_3$

centred about the point $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

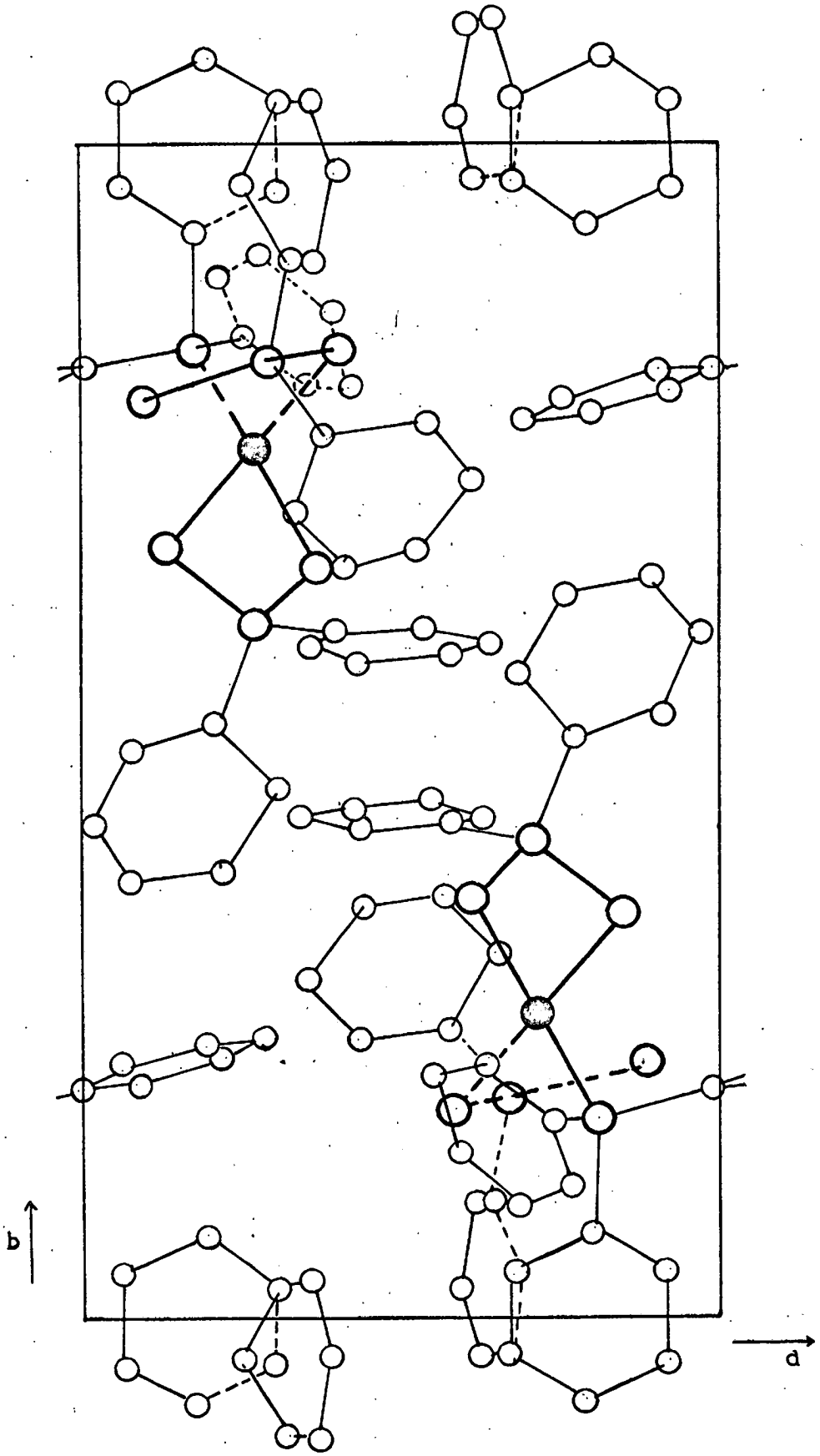


Figure 3.4b

TABLE 3.4

Bond distances in Å for $Pd(S_2PPh_2)_2PPh_3$

	Pd-S2	2.416(9)	
	Pd-S3	2.369(9)	
	Pd-S1	2.331(9)	
	Pd-S4	3.485(11)	
	Pd-P2	2.274(8)	
Monodentate Ligand		Bidentate Ligand	
S1-P3	2.047(10)	S2-P1	1.986(11)
S4-P3	1.966(13)	S3-P1	2.017(12)
P3-C1	1.808(25)	P1-C13	1.756(27)
P3-C19	1.740(31)	P1-C31	1.835(39)
C1-C2	1.466(39)	C13-C14	1.359(50)
C2-C3	1.514(44)	C14-C15	1.629(63)
C3-C4	1.291(48)	C15-C16	1.258(82)
C4-C5	1.448(52)	C16-C17	1.285(67)
C5-C6	1.367(47)	C17-C18	1.375(55)
C6-C1	1.397(37)	C18-C13	1.428(52)
C19-C20	1.417(57)	C31-C32	1.406(71)
C20-C21	1.408(63)	C32-C33	1.673(85)
C21-C22	1.477(63)	C33-C34	1.453(110)
C22-C23	1.241(94)	C34-C35	1.279(139)
C23-C24	1.365(82)	C35-C36	1.341(108)

Table 3.4 page 2

Monodentate Ligand		Bidentate Ligand	
C24-C19	1.433(49)	C36-C31	1.357(76)

Phosphine Distances

P2-C7	1.830(24)	C27-C28	1.439(61)
P2-C25	1.751(29)	C28-C29	1.515(52)
P2-C37	1.796(26)	C29-C30	1.446(50)
C7-C8	1.384(43)	C30-C25	1.462(39)
C8-C9	1.400(40)	C37-C38	1.380(39)
C9-C10	1.401(49)	C38-C39	1.506(45)
C10-C11	1.374(51)	C39-C40	1.320(46)
C11-C12	1.385(41)	C40-C41	1.462(44)
C12-C7	1.407(41)	C41-C42	1.445(49)
C25-C26	1.354(41)	C42-C37	1.389(43)
C26-C27	1.354(59)		

TABLE 3.5

Bond angles in degrees for $Pd(S_2PPh_2)_2PPh_3$

About the metal atom

S2-Pd-S3	83.6(3)	Pd-S3-P1	83.1(4)
S2-Pd-S1	92.9(3)	Pd-S1-P3	99.6(4)
S1-Pd-P2	95.6(3)	Pd-P2-C7	121.7(8)
P2-Pd-S3	87.9(3)	Pd-P2-C25	109.2(8)
S2-Pd-P2	169.3(2)	Pd-P2-C37	110.1(9)
S1-Pd-S3	176.5(4)	Pd-P1-C13	145.4(10)
Rd-S2-P1	82.5(4)	Pd-P1-C31	109.7(11)

Monodentate Ligand		Bidentate Ligand	
S1-P3-S4	116.3(5)	S2-P1-S3	105.7(4)
S1-P3-C1	103.7(9)	S2-P1-C13	113.9(10)
S1-P3-C19	106.6(11)	S2-P1-C31	111.5(13)
S4-P3-C1	111.8(10)	S3-P1-C13	111.8(11)
S4-P3-C19	112.3(11)	S3-P1-C31	109.1(12)
C1-P3-C19	105.3(13)	C13-P1-C31	104.8(14)
P3-C1-C2	117.0(18)	P1-C13-C14	116.8(26)
P3-C1-C6	118.6(19)	P1-C13-C18	123.0(23)
C2-C1-C6	123.5(23)	C14-C13-C18	120.1(29)
C1-C2-C3	110.0(24)	C13-C14-C15	112.0(37)
C2-C3-C4	126.2(31)	C14-C15-C16	121.8(46)

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C3-C4-C5	118.4(31)	C15-C16-C17	121.8(47)
C4-C5-C6	121.5(33)	C16-C17-C18	123.2(44)
C5-C6-C1	119.3(27)	C17-C18-C13	120.5(36)
P3-C19-C20	120.6(24)	P1-C31-C32	115.8(30)
P3-C19-C24	122.0(27)	P1-C31-C36	119.3(40)
C20-C19-C24	117.3(32)	C32-C31-C36	123.5(46)
C19-C20-C21	123.7(36)	C31-C32-C33	110.4(41)
C20-C21-C22	118.8(41)	C32-C33-C34	109.2(61)
C21-C22-C23	124.9(49)	C33-C34-C35	135.6(81)
C22-C23-C24	124.2(57)	C34-C35-C36	109.6(74)
C23-C24-C19	118.0(45)	C35-C36-C31	127.9(70)

Phosphine Angles

C7-P2-C25	106.1(12)	C26-C25-C30	114.0(26)
C7-P2-C37	101.9(11)	C26-C27-C28	123.3(36)
C25-P2-C37	106.8(12)	C27-C28-C29	114.4(36)
		C28-C29-C30	117.3(30)
P2-C7-C8	122.2(20)	C29-C30-C25	123.8(25)
P2-C7-C12	117.6(20)		
C8-C7-C12	120.3(23)	P2-C37-C38	118.7(21)
C7-C8-C9	121.9(28)	P2-C37-C42	120.0(20)
C8-C9-C10	117.6(30)	C38-C37-C42	121.2(25)

C9-C10-C11	119.5(28)	C37-C38-C39	120.5(28)
C10-C11-C12	123.8(32)	C38-C39-C40	114.9(27)
C11-C12-C7	116.7(28)	C39-C40-C41	127.8(29)
		C40-C41-C42	113.8(30)
P2-C25-C26	129.2(22)	C41-C42-C37	121.2(27)
P2-C25-C30	116.8(22)		

3.6 Discussion of the Structure

In bis(diphenylphosphinodithioato)triphenylphosphinepalladium (II) the palladium atom is four coordinate in the solid state, as shown in Figure 3.3. The palladium is coordinated to both sulphur atoms of one phosphinodithioato-ligand, and to one sulphur of the other ligand. The fourth coordinate bond is to the phosphorus of triphenyl phosphine. The remaining sulphur atom of the monodentate phosphinodithioato-ligand is not bonded to the palladium. A structure of this type was inferred from studies of the i.r. spectra (see Chapter 2). A very similar structure has also been found for $Pt(p\text{-dithiocumato})_2PMePh_2$[70].

The palladium-sulphur bond distances associated with the two sulphur atoms cis to the phosphine group are closely similar at 2.331(9) Å and 2.369(9) Å (Table 3.4). These bond distances fall slightly outside the range of palladium-sulphur bond distances reported for bis(dithiobenzoato)palladium as 2.32-2.34 Å[71]. However, a similar small increase in nickel-sulphur distances for the complexes $Ni(S_2PR_2)_2$ compared with the complexes $Ni(S_2CR_2)_2$ or $Ni(S_2CNR_2)_2$ has been generally observed, the increase being about 0.02 Å[5].

In $Pd(S_2PPh_2)_2PPh_3$ the shorter palladium-sulphur bond is that associated with the monodentate phosphinodithioato-ligand although the calculated difference in bond distances may not be significant. In $Pt(p\text{-dithiocumato})_2PPh_2Me$ the platinum-sulphur bonds cis to the phosphine were found to be equivalent at 2.312(3)

and 2.305(2) Å for the monodentate and bidentate ligands respectively [70]. In $Au(S_2CNEt_2)_3$ where two of the dithiocarbamate ligands are monodentate, the metal-sulphur distances associated with the chelate and monodentate ligands are all within the same range [72]. The ruthenium-sulphur distance associated with the monodentate ligand in $Ru(NO)(S_2CNEt_2)_3$ [73] is shorter than the average ruthenium-sulphur bond distance of the chelate ligands, but as these vary widely the observation may be of small significance.

The palladium-sulphur bond distance associated with the sulphur trans to the phosphine is longer at 2.416(9) Å. This lengthened bond distance is probably due to the trans influence of the tertiary phosphine. The palladium-phosphine distance of 2.274 Å is significantly shorter than the 2.41 Å obtained from covalent radii [74] and strongly indicates some palladium-phosphorus π-interaction. Similar lengthening of the metal-sulphur bond of the chelate ring trans to the phosphine was observed in Pt(p-dithiocumato)$_2$PPh$_2$Me [70] where a platinum-sulphur bond distance of 2.390 Å was observed and in $[Pd(S_2PPh_2)(PEt_3)]S_2PPh_2$ where both sulphur atoms are trans to tertiary phosphines the distance is 2.41 Å [58].

The palladium atom and the four atoms bonded to the palladium are not strictly planar, but deviations from planarity are less than 0.081 Å. Table 3.6 lists the plane for these atoms and some other least squares planes for the molecule. The non-bonded palladium-sulphur distance is 3.485 Å and is close to that reported for the non-bonded platinum-sulphur distance in Pt(p-dithiocumato)$_2$PPh$_2$Me

(3.580(3) Å). The perpendicular distance of the free sulphur atom to the $PdS^1S^2S^3P^2$ plane is 3.29 Å. The distance from the palladium to the point of projection of the free sulphur onto the plane is 1.285 Å. The palladium-sulphur direction forms an angle of 68° with the plane, and thus the sulphur atom is not near the apical position of a square pyramid. The palladium-sulphur distance is even longer than the palladium sulphur contact distance of 3.46 Å quoted for bis(dithiobenzoato)palladium where the interacting sulphur atoms occupy apical positions of distorted square pyramidally and octahedrally coordinated palladium atoms[71]. It therefore seems unlikely that any interaction between the palladium and free sulphur atom occurs in $Pd(S_2PPh_2)_2PPh_3$.

The geometry around the palladium atom is distorted from square planar as the angles deviate slightly from 90° (Table 3.5). This distortion is chiefly due to the S-Pd-S angle of 83.6° caused by the four-membered chelate ring. This angle is smaller than that found for the nickel bis phosphinodithioates or dithiophosphates[5,6] but is larger than the S-Pd-S angle of 81.9° found in $[Pd(S_2PPh_2)(PEt_3)_2]S_2PPh_2$.

A least squares plane calculated for $PdS^2P^1S^3$ (Table 3.6) shows that the chelate ring is definitely non planar. Similar non planarity was found in the $[Pd(S_2PPh_2)(PEt_3)_2]$ cation. The phosphorus-sulphur distances are close to those found in the nickel bis chelate systems, and indicate some double bond character due to electron delocalisation around the chelate ring. The phosphorus-

sulphur bond associated with the sulphur trans to the phosphine group is slightly shorter and this is consistent with the lengthened metal-sulphur bond. However, the difference in calculated bond lengths is hardly significant. The S-P-S angles are within previously reported ranges and all the angles at the phosphorus atom are close to tetrahedral.

In the monodentate phosphinodithioato-ligand the Pd-S-P angle is increased from close to 83° to 99.6(4)°, and the S-P-S angle is increased from 105.7(4)° to 116.3(5)°. The sulphur-sulphur 'bite' distance is lengthened to 3.408 Å in the monodentate ligand compared with 3.19 Å in the bidentate ligand. Both phosphorus-sulphur bond distances show some double bond character. The phosphorus-sulphur distance of the uncoordinated sulphur atom (1.966(13) Å) is significantly shorter than the other (2.047(10) Å). The C-P-C angle is unchanged in the monodentate ligand.

All the phenyl groups are poorly resolved. They are approximately planar (Table 3.6) but the carbon-carbon bonds range from 1.24(9) Å to 1.67(8) Å with ring angles of 109° to 133°.

TABLE 3.6

Some least squares planes for $Pd(S_2PPh_2)_2PPh_3$

The table shows the equation of the plane [a], and distances of the atoms from the plane.[b] Atoms marked * were not included in the plane calculation.

PLANE 1

P = -7.0120 Q = 0.5723

R = 15.3588 S = -0.5118

Pd	-0.051
S1	-0.050
S2	0.080
S3	-0.061
P2	0.082
*S4	-3.290
*P1	0.569
*P3	-1.985

σ = 0.074

PLANE 2

P = -6.7253 Q = -3.0484

R = 15.4667 S = -1.5436

Pd	0.124
S2	-0.156
S3	-0.157
P1	0.189
*S1	0.370
*S4	-2.936
*P2	0.603
*P3	-1.587

σ = 0.183

PLANE 3

P = -1.2626 Q = 5.7039

R = 20.8621 S = 3.9105

P1	-0.060
C13	0.033
C14	0.082
C15	-0.054
C16	-0.038

PLANE 4

P = 0.0032 Q = 18.4173

R = -3.0991 S = 7.2618

P1	0.013
C31	0.060
C32	-0.012
C33	-0.019
C34	0.005

Table 3.6 page 2

PLANE 3

C17	0.031
C18	0.006

σ = 0.053

PLANE 4

C35	0.071
C36	-0.118

σ = 0.062

PLANE 5

P = 0.0389 Q = -5.0694

R = 21.3655 S = 1.5549

P2	0.018
C7	-0.009
C8	-0.038
C9	0.034
C10	-0.001
C11	-0.004
C12	0.000

σ = 0.023

PLANE 6

P = -2.5447 Q = 18.0215

R = -2.5849 S = 1.9142

P2	0.034
C25	-0.012
C26	-0.036
C27	0.025
C28	0.003
C29	0.024
C30	-0.038

σ = 0.030

PLANE 7

P = 6.6693 Q = 10.1143

R = 9.5815 S = 5.0514

P2	-0.087
C37	0.035
C38	0.069
C39	-0.004
C40	-0.073
C41	-0.024
C42	0.084

σ = 0.066

PLANE 8

P = 9.2080 Q = 0.6641

R = -6.7724 S = 2.4144

P3	0.020
C1	-0.066
C2	0.047
C3	-0.034
C4	0.016
C5	0.016
C6	0.001

σ = 0.038

Table 3.6 page 3

PLANE 9

P = -1.5314 Q = 9.2801

R = 18.8544 S = -0.1693

P3	0.056
C19	-0.044
C20	-0.021
C21	-0.002
C22	0.033
C23	0.031
C24	-0.053

σ = 0.042

[a] The form of the plane equation is $Px + Qy + Rz = S$ in cartesian coordinates, where x, y and z are the fractional coordinates of the atoms in the direct cell.

[b] in Å.

TABLE 3.7 page 1

Structure factors (F_{obs}, F_{calc}) for $Pd(S_2PPh_2)_2PPh_3$

0,0,L

4	1447	-1619
6	2058	-2530
8	1996	-2047
12	585*	392
14	1227	1024
16	1668	1640
18	909	789

0,1,L

-22	1093	1111
-20	1018	923
-18	704*	546
-16	1005	-724
-14	1437	-1240
-10	1091	943
-8	695*	-272
-6	443*	-45
-4	867	622
4	1533	-1782
6	1247	-1197
8	662	-419
10	794	679
14	1605	1656
16	1238	1067
20	1257	-1157
22	839	-921

0,2,L

-20	673*	-513
-18	1220	-1091
-16	1979	-1956
-14	957	-727
-12	679*	359
-10	790	577
-8	1125	1106
-6	503	-312
-4	711	-216
-2	1038	-1926
2	580	-549
4	1190	1288
6	612*	-286
8	495	-436
10	885	809
12	534*	386
16	714*	-441
18	916	-870

0,3,L

-24	732*	-871
-22	992	-1112
-20	982	-946
-16	1130	705
-14	1758	1580
-12	897	766
-8	1491	-1216
-6	1757	-1688
-4	1598	-1472
0	762	-751
2	816	728
4	1076	1040
6	2519	3267
8	1186	941
10	1186	-1016
12	1649	-1658
14	2225	-2564
16	1530	-1505
20	1077	1142
22	788*	869

0,4,L

-18	743*	664
-16	1422	1289
-14	1568	1301
-10	2068	-2095
-8	2345	-2573
-6	1865	-1593
-4	1253	1104
0	1123	1163
2	1595	2009
4	1950	-2053
6	1707	-2048
8	1682	-1952
10	1660	-1753
16	823	755

0,5,L

-24	990	1177
-18	1065	-832
-10	589	-377
-8	619	484
-6	1274	1165
-4	370*	-45
-2	1600	1599
0	2077	3122
4	663	-645
6	1948	-2341
8	460*	-352
10	2147	2404
12	2004	2127
14	1116	1018
18	783*	-434

0,6,L

-12	1446	1317
-10	2383	2348
-8	1959	2003
-6	702	531
-4	1099	-990
-2	580	359
0	1208	-1100
2	635	-532
4	1080	966
6	1865	1926
8	1610	1605
10	1559	1474
14	669*	-493

0,7,L

-24	771	-942
-22	701*	-712
-12	1200	1130
-10	902	738
-6	1648	-1721
-4	1603	-1629
-2	1424	-1424
0	1283	-1167
2	550	-288
4	1691	1982
6	2049	2179
10	1839	-1934
12	1936	-2152
20	740	782
22	760	858

0,8,L

-24	542*	-669
-18	919	899
-12	1452	-1366
-10	1989	-1878
-8	1375	-1391
-4	1290	1182
-2	1526	1648
8	870	-680
10	769	-617
12	848	-836
16	915	870
18	797*	694

0,9,L

-22	635*	679
-16	817	-729
-14	790*	-820
-12	1196	-1047
-10	597*	-290
-8	1192	953
-6	1183	1070
-4	1401	1269
-2	1094	-877
2	1784	-1987
4	1471	-1503
6	835	-778
10	616*	304
18	1040	-884
20	1036	-1096
22	724	-863

0,10,L

-20	1104	-1128
-18	1063	-1214
-16	784	-636
-14	867	723
-12	1290	1182
-10	707	639
-8	638*	343
-4	1090	-901
-2	1151	-984
0	1313	-1070
2	1147	-956
4	557*	356
8	564*	480
10	970	911
12	869	753
16	1274	-1295
18	1014	-945
22	568*	640

0,11,L

-18	785	742
-16	1073	1029
-14	822	499
-10	624*	315
-8	809	598
-4	809	-624
-2	1012	-775
0	777	611
2	1977	2302
4	2014	2154
6	1222	1127
12	868	-781
14	881	-845
18	957	1007
20	795	914

0,12,L

-20	1072	1160
-18	1044	1141
-14	751*	-474
-12	923	-851
-8	665*	235
-2	1204	1095
0	1488	1392
2	594*	514
4	1046	-959
6	644*	-609
8	692*	-639
10	900	-796
14	740*	566
16	1206	1275
18	744*	844

0,13,L

-16	1093	-1057
-14	1100	-1044
-12	895	-915
-10	732*	-487
-6	1345	1157
-4	1545	1419
0	1777	-1661
2	1745	-1809
4	1054	-953
8	895	642
10	763*	627

0,14,L

-18	658	-785
-12	862	750
-10	763*	517
-4	727	-456
-2	1527	-1457
0	1200	-1052
4	868	821
6	948	898
14	699*	-640
16	718*	-892
18	675*	-875

0,15,L

-14	938	923
-8	1117	-1020
-6	1574	-1612
-4	673*	-600
10	1027	-1020
12	1013	-1043
14	712	-776

0,16,L

-12	806	-796
-10	1301	-1304
-4	935	938
-2	805	764
2	789*	640
8	758*	-648
14	887	864
16	591*	769

0,17,L

-10	796	654
-8	1430	1461
-6	1236	1141
4	814*	-774
8	692*	550
10	1126	1119
12	1041	1025

0,18,L

-10	877	899
-2	739*	-674
0	905	-856
2	769*	-753
6	1049	1044
8	1138	1140
12	684*	-635
14	655	-810

0,19,L

-8	743	-777
-6	718*	-637
4	1109	1223
10	905	-924
12	658	-711

0,20,L

-10	506*	-800
-4	672*	552
-2	749	823
4	709	-717
6	908	-972

0,21,L

-6	781	642
0	812	-924
2	853	-903
4	652	-682

1,-19,L

-7	1208	1119
-5	950	942
-1	540*	-416
1	924	-881
3	767	-755
5	557*	-471

1,-18,L

-9	722	743
-5	685	-624
1	781	-725
5	724	751
7	842	948
9	730	678

1,-17,L

-9	1000	-924
-7	1032	-996
-3	745	618
-1	886	830
1	799	781
3	1029	973
5	1147	944
9	897	-427

1,-16,L

-13	622	-476
-11	1030	-962
-9	569*	-509
5	1168	-1015
7	1478	-1440
9	1030	-1002
13	615	669

1,-15,L

-15	1233	-1278
-13	636	-665
-7	573*	516
-1	887	-888
1	967	-939
9	648	549
11	692	731

1,-14,L

-11	551*	505
-9	799	737
-7	960	860
-3	1035	-945
-1	1853	-1448
1	1177	-1162
5	1653	1572
7	1256	1304
13	1062	-1103
15	968	-1041

1,-13,L

-17	1219	1252
-15	770	805
-9	679	-544
-7	1163	-1126
-5	1414	-1295
-3	518*	-396
-1	1206	1176
1	1252	1240
3	598	563
5	726	-519
9	790	-606
11	1311	-1332
13	985	-946
17	659	726

1,-12,L

-11	657	-643
-9	1362	-1386
-7	726	-601
-5	888	836
-3	2197	2367
-1	2213	2485
3	1489	-1454
5	732	-696
9	997	829
11	558*	318
13	957	895
15	1436	1326
17	704	751

1,-11,L

-17	1228	-1224
-15	681	-672
-11	1100	978
-9	1121	1135
-7	1166	1236
-5	1312	1227
-1	666	-575
1	1234	-1069
3	432*	244
5	618	596
7	757	-650
11	1132	1060
13	1351	1376
15	551*	441
17	621*	-657
19	875	-1010

1,-10,L

-19	804	-740
-17	1115	-1072
-13	697	706
-11	721	616
-9	735	672
-5	1218	-1207
-3	2094	-2294
-1	2031	-2149
3	1384	1208
5	789	763
7	628	345
11	764	-514
13	818	-794
15	1323	-1375
17	868	-854

1,-9,L

-17	834	727
-15	890	747
-13	932	-715
-11	1057	-1069
-9	640	-669
-7	1210	-1098
-5	429*	-369
-3	1109	-1070
1	799	652
3	1877	2054
5	1076	960
9	1340	-1353
11	1747	-1804
13	1078	-876
17	1163	1215
19	1057	1187

1,-8,L

-21	711	652
-19	604*	484
-17	695	630
-15	606*	586
-13	882	-799
-11	1437	-1385
-9	761	-639
-5	1498	1591
-3	1144	1040
-1	801	695
1	1047	942
3	1026	-915
5	2416	-3010
7	1558	-1583
9	636	-442
11	912	734
13	575*	509
21	520*	-591

* These reflections were treated as unobserveds.

TABLE 3.7 page 2

	1,-7,L			1,-2,L		-9	1783	-1614		1,10,L		0	1075	988
						-7	1610	-1525				2	919	994
-17	863	-808	-23	556*	-619	-5	926	740	1	703	643	6	887	-843
-11	555	380	-21	1417	-1364	-3	1828	2048	3	1216	1385	8	823	-697
-9	741	583	-19	944	-856	1	949	966	5	1024	914			
-7	823	810	-17	953	878	3	1159	-1132	7	1039	1083		2,-16,L	
-3	456	288	-15	1453	1382	5	296*	-274	13	1253	-1173			
-1	864	730	-13	949	682	7	1747	-1971	15	873	-727	-14	1286	-1242
1	812	-771	-11	499	329	9	1978	-2485	17	640	519	-12	771	-718
3	2207	-2593	-7	1331	-1295	11	1179	-1120	19	1392	1075	-10	700	628
5	1340	-1151	-1	327	339	13	740	-704				-8	918	887
7	930	869	5	823	-562	17	567*	526		1,11,L		-4	486*	-294
9	2288	2312	7	598	442	19	676	669				-2	917	-899
11	1555	1679	9	1042	797	23	671	-648	-1	1800	2092	0	726	-660
13	579	563	11	749	578				1	1668	1702	2	1033	-956
15	613	-575	13	1692	-1667		1,4,L		3	838	655	4	919	-914
17	787	-771	15	2207	-2231				7	486*	-456			
19	628*	-716	17	1049	-992	-19	970	933	9	1209	-1223		2,-15,L	
			21	1029	1057	-15	1134	-1114	11	656	-554			
	1,-6,L		23	571*	724	-13	1705	-1652	15	1447	1424	-2	772	-771
						-11	1501	-1464	17	1457	1563	0	979	-849
-17	802	-620		1,-1,L		-9	652	575				2	1415	-1381
-15	548*	-387				-7	1272	1122		1,12,L		6	1048	1140
-13	1872	1917	-19	1038	1067	-5	732	616				8	1197	1255
-11	2625	3181	-17	863	793	-1	1548	-1650	1	1194	-1108	10	651*	733
-9	1147	1017	-11	813	567	1	1558	2018	3	1418	-1432	12	725	-646
-7	1265	-1208	-5	2158	-3445	3	1296	-1528	5	863	-850	14	803	-831
-5	1397	-1533	-7	1604	-1713	5	1629	-1867	11	818	723			
-3	351*	22	7	884	-756	7	1535	-1669	13	1073	1009		2,-14,L	
1	438	-56	15	1536	1347	11	1208	1128	15	714	695			
3	2004	2367	17	1566	1518	13	1092	1138				-18	759	906
5	2570	3119	19	620*	619	15	1175	1164		1,13,L		-16	1015*	910
7	1167	1047				21	867	-947				-14	499*	533
9	767	500		1,0,L					1	1114	-1041	-8	741*	-558
15	535*	196					1,5,L		5	876	822	-6	899	-873
17	980	-1028	-23	923	1016				7	818	815	-4	731	-656
21	530*	658	-21	1479	1678	-15	1052	-929	9	966	925	-2	563*	421
			-19	1073	937	-11	1530	1436	15	606*	-473	0	909	937
	1,-5,L		-17	584*	-509	-9	2281	2495				4	969	960
			-15	653	-623	-7	1628	1555		1,14,L		6	844	668
-21	577*	565	-13	1199	-1017	-1	382	297				10	882	-858
-15	1076	889	-9	403	378	1	521	-564	1	740	596	12	1040	-1458
-13	1254	1038	-7	2068	2206	3	728	-635	3	888	791	14	728	-691
-11	599	452	-5	2872	4764	5	1476	1664	5	595*	488			
-9	443*	-62	-3	1462	1613	7	2119	2516	9	598	-575		2,-13,L	
-7	1356	-1237	5	1187	-1148	9	1716	1862	11	1251*	-1126			
-5	866	-723	7	824	704	11	866	781	13	904	-961	-10	816	-754
-3	377	267	11	712	606	15	522*	417	15	973	-883	-8	1383	-1282
-1	1319	-1165	13	1568	1488							-6	802	-665
1	1510	1702	15	1543	1374		1,6,L			1,15,L		-4	1147	971
3	1822	2109	17	610	558							-2	1797	1955
5	1163	904	19	552*	-518	-13	1336	1256	5	839	-819	0	808	757
7	1900	-1829	21	794	-798	-11	1279	1247	7	1077	-992	2	643	-509
9	1904	-1796				-1	1202	-1198	9	896	-792	4	1127	-1018
11	1674	-1587		1,1,L		3	1555	1850				6	1228	-1233
15	546*	353				5	2284	3132		1,16,L		8	720	-726
19	1062	1063	-19	787	-756	7	913	869				12	837	635
21	575*	652	-17	1025	-1013	9	1507	-1661	5	808	-701	14	1376	1357
			-15	719	-587	11	1586	-1724	9	816	781	16	676	717
	1,-4,L		-13	1074	-887	13	1057	-1013	11	1380	1122			
			-11	892	-390	21	1021	600	13	907	982		2,-12,L	
-21	860	888	-9	630	516									
-15	1210	-1026	-7	1617	1666		1,7,L			1,17,L		-18	790	-900
-13	2176	-2336	-5	2188	2818							-16	1071	-1141
-11	2630	-3278	-3	1723	-2102	-1	1266	1342	5	691	689	-10	595*	509
-9	590	-440	5	471	-303	1	1227	1206	9	804	717	-8	1691	1657
-7	1048	965	7	957	865	3	607	585				-6	1805	1852
-5	1109	1239	11	776	457	5	813	-723		1,18,L		-4	911	740
1	1043	-1129	15	1040	-818	7	1668	-1758				-2	738	-641
5	1746	-1703	17	641	-609	9	1358	-1361	9	848	-933	2	711	616
7	819	-764	19	545*	-433	11	455*	-343				0	840	-851
11	514	400				15	742	710		1,17,L		4	933	695
13	742	578		1,2,L		17	823	859				10	840	839
15	878	805				19	618*	677	7	1093	1039	12	1376	1362
17	685*	506	-21	1229	-1375	21	671	560				14	926	935
21	839	-840	-19	855	-809					2,-20,L		20	504*	-440
23	715	-829	-15	1300	1147		1,8,L							
			-13	636	616				-8	433*	351		2,-11,L	
	1,-3,L		-11	857	-617	-1	645	562						
			-9	1293	-1040	1	1142	-1032		2,-19,L		-20	428*	-516
-21	615*	-576	-7	1093	-968	3	1606	-1751				-18	663	-711
-19	1101	-1285	-5	915	-787	5	1236	-1289	0	966	-1036	-12	585*	528
-17	1028	-959	-3	1265	-1197	7	557	-481	2	667	-762	-10	1491	1519
-15	710	-554	3	625	-535	9	640	569	6	820	881	-8	1408	1311
-13	549	429	5	646	522	11	680	582				-4	1546	-1578
-11	868	722	7	670	580	13	503*	396		2,-18,L		-2	2013	-2255
-9	826	581	9	1212	1164	15	597*	422				0	433*	-242
-7	925	929	13	1119	-1013	19	682	-662	-8	1113	-1009	2	1097	983
-5	1267	1350	15	1576	-1596	21	1139	-943	-6	853	-894	4	596	500
-3	997	-1027	17	650	-555				-4	638*	-378	8	437*	340
-1	1402	-1898	19	660	556		1,9,L		-2	520*	461	10	468*	444
1	515	377	21	891	896				2	998	1042	14	1121	-1130
3	2808	-3876	23	634	625	-1	1480	-1605	4	1272	1223	16	808	-896
5	1341	-1188				13	630	-468						
7	885	787		1,3,L		15	1072	-1080		2,-17,L			2,-10,L	
9	2043	2045				17	1183	-1177						
11	2049	1998	-19	847	852	19	1037	-868	-12	701	-693	-22	1016	-1083
15	1387	-1254	-17	1648	1585				-10	743*	-725	-18	603*	694
17	1485	-1464	-15	1493	1333				-6	621*	588	-16	919	1027
19	1309	-1287	-11	1791	-1733				-2	768	817	-12	902	-756

* These reflections were treated as unobserveds.

TABLE 3.7 page 3

	2,-10,L	
-10	1116	-1085
-8	1584	-1511
-6	1149	-1044
-4	753	-755
2	426*	-362
6	506*	364
10	1052	-1088
12	1445	-1386
14	772	-757
18	913	952
20	804	976
	2,-9,L	
-20	817	745
-18	597*	658
-16	517*	218
-14	1085	-1106
-12	1174	-1143
-10	1165	-1042
-8	763	-555
-6	585	408
-4	1352	1354
-2	1963	2266
0	867	848
2	909	-659
4	826	-843
6	1402	-1352
8	1207	-1026
12	593*	613
14	822	834
	2,-8,L	
-24	781	1020
-22	525*	768
-18	910	-722
-16	1380	-1386
-12	777	758
-10	1185	1092
-8	480*	413
-2	583	571
0	1003	-976
2	1148	-1022
4	1935	-2092
6	934	-919
8	757	597
10	1470	1464
12	704	623
16	778	-799
18	1076	-1152
20	626*	-721
	2,-7,L	
-18	990	-1024
-16	1029	-962
-14	1206	1274
-12	1772	1898
-10	1365	1295
-8	586	461
-6	1230	-1208
-4	643	-615
-2	1178	-1159
0	989	-1024
2	1120	1060
4	2114	2268
6	1627	1788
8	653	577
10	475*	-462
14	671	472
22	701	801
	2,-6,L	
-18	780	624
-16	787	661
-14	1266	1037
-12	742	577
-8	833	-806
-6	651	-392
-4	586	410
0	1634	2018
2	2267	2912
4	2607	2901
8	1845	-1857
10	1119	-1012
14	531*	347
18	552*	577
20	908	1032
22	555*	535
	2,-5,L	
-20	566*	584
-18	1257	1291
-16	1089	972
-14	1048	-829
-12	2402	-2563
-10	1937	-2059
-6	647	525
-4	1297	1327
-2	932	928
0	597	541
2	2048	-2342
4	2176	-2359
6	1964	-2353
16	543*	465
18	831	807
24	764	-933
	2,-4,L	
-20	651*	-569
-18	719	-756
-16	1400	-1442
-14	1391	-1407
-12	774	-759
-10	597	543
-8	1359	1435
-6	420	410
-4	286*	-88
-2	369	-186
0	1482	-1857
2	1770	-2144
4	889	-758
6	308*	2
8	1381	1443
10	1240	1075
16	601*	-403
18	749	-715
20	1384	-969
	2,-3,L	
-22	803	-946
-20	1074	-1099
-18	732	-621
-14	1679	1681
-12	1593	1567
-10	1079	934
-8	1173	-1102
-6	869	-905
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2	1095	1141
4	866	686
6	1108	907
8	805	570
10	663	339
12	1275	-1174
14	1800	-1750
16	1535	-1457
18	694	-576
	2,-2,L	
-24	534*	-641
-20	744	670
-18	826	788
-16	856	819
-14	511*	523
-10	828	789
-8	1096	-1017
-6	1833	-2187
-4	961	-901
-2	1262	-1396
4	1065	1063
6	901	806
8	1914	-1850
10	2200	-2406
12	1203	-1204
16	1452	1432
18	1277	1195
20	592*	668
	2,-1,L	
-24	433*	493
-22	1066	1209
-20	1038	1070
-16	528*	-437
-14	531*	-541
-12	692	-572
-10	746	-642
-8	610	-416
-6	1685	1828
-4	2154	3332
4	675	562
6	431*	76
8	1064	-1059
10	788	612
12	1759	1685
14	2121	2302
16	1350	1252
	2,0,L	
-24	592	739
-18	758	-647
-12	379*	-390
-10	735	-471
-8	2639	2861
-6	2442	3205
-4	1365	1339
6	705	709
8	1124	1079
10	1562	1451
12	1112	986
14	714	-575
16	1104	-977
18	826	-746
	2,1,L	
-24	469*	-637
-22	1085	-1235
-20	1005	-1021
-14	492*	528
-10	489	370
-8	927	700
-6	1742	-1909
-4	2048	-2414
4	762	-592
6	1101	1010
10	300*	-262
12	858	-747
14	1493	-1478
16	895	-782
20	512*	518
	2,2,L	
-22	627*	-647
-16	586*	544
-14	521*	499
-10	1253	-1319
-8	1588	-1584
-6	1667	-1770
4	531*	-87
6	421	431
8	1079	-996
10	1770	-1790
12	662	-657
18	855	818
20	799	672
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-22	795	906
-20	902	959
-18	821	605
-14	1445	-1398
-12	1400	-1304
-10	470*	246
-8	318*	155
-6	1017	889
-4	1364	1214
2	1235	-1123
4	1381	-1578
6	1493	-1484
8	1549	-1643
10	440*	-372
12	884	743
14	688	692
16	605*	624
20	1282	-1004
	2,4,L	
-18	1014	-1042
-16	1440	-1418
-14	766	-636
-12	1047	1024
-10	1626	1570
-8	1221	1155
-6	997	850
2	1898	-2432
4	325*	-238
6	301*	125
8	1794	2117
10	1824	1925
12	1020	990
14	516*	445
16	912	-843
20	1024	-794
	2,5,L	
-16	778	676
-14	1533	1490
-12	1535	1439
0	734	521
2	689	678
4	2330	3067
6	1760	2037
8	1068	938
10	760	-576
12	740	-635
20	589*	508
	2,6,L	
-16	758	798
-14	761	564
-12	848	-629
-10	1029	-825
0	1046	1041
2	1552	1966
6	1464	-1508
8	1810	-2051
10	1041	-1039
12	426*	-361
16	609*	523
18	802	746
	2,7,L	
-2	1217	1362
0	448	365
2	1358	-1537
4	2196	-2627
6	929	-885
10	842	881
12	780	694
16	808	659
18	603*	504
	2,8,L	
0	1313	-1402
2	1162	-1153
4	616	-537
6	1196	1228
8	805	759
10	869	888
14	1273	-1337
16	1015	-1045
18	1396	-1002
	2,9,L	
0	845	827
2	889	838
4	750	-590
6	429*	-233
8	438*	354
12	727	-662
14	1467	-1477
16	674*	-579
	2,10,L	
0	1484	1474
2	1315	1434
4	774	657
6	562*	403
8	625	-509
10	1037	-909
14	921	907
16	1852	1806
18	999	1068
	2,11,L	
2	496*	-436
6	437*	-394
8	905	-951
12	1437	1291
14	1339	1522
16	581*	344
	2,12,L	
2	932	-933
6	793	685
8	1070	1143
10	917	864
14	1083	-947
16	1425	-1209
	2,13,L	
4	894	962
6	635*	503
8	595	584
12	969	-994
14	1149	-1076
	2,14,L	
4	886	-855
6	1664	-1588
8	1047	-1124
10	740	-609
	2,15,L	
6	739	-617
10	590*	457
	2,16,L	
8	1589	1081
	3,-16,L	
1	828*	-1084
15	661*	-614
	3,-15,L	
3	1259	1175
	3,-14,L	
-7	843*	-900
-1	2092	1793
1	1312	1199
5	1116	-1267
7	2130	-1811
9	1368	-1428
	3,-13,L	
-7	1108	1138
-5	959	1093
9	782*	855
11	1404	1548
13	923	1042
	3,-12,L	
-11	1231	1095
-9	2642	2000
-7	1334	1323
-5	661*	-651
-3	1924	-1750
1	635*	642
5	1032	1194
7	865*	975
9	787*	1083
	3,-11,L	
-9	677*	-634
-7	2208	-2092
-5	1302	-1267
11	1349	-1371
13	1411	-1464
	3,-10,L	
-11	1333	-1268
-9	1607	-1630
-7	1119	-1241
-3	1209	1188
-1	682*	689
7	1101	-1172
9	744*	-990
15	798*	1093
	3,-9,L	
-15	1206	-1090
-9	1231	1087
-7	784*	729
-3	595*	634
1	754	-708
3	1523*	-1374
5	790	-943
11	1152	1257
13	743*	817
17	964	-1042
19	1337	-1256
	3,-8,L	
-13	1485	1514
-11	831*	1019
-3	793	-845
-1	1738	-1603
1	1060	-1121
5	1737	1579
7	1206	1121
9	598*	573
17	820*	-942
	3,-7,L	
-5	761	-827
1	1464	1394
3	3016	2947
5	1865	1651
19	921*	1165
21	688*	973

* These reflections were treated as unobserveds.

TABLE 3.7 page 4

	3,-6,L	
-11	1003	-995
-5	998	897
-3	1844	1760
-1	2528	2560
1	432*	464
3	1488	-1486
5	1910	-1627
7	1209	-992
15	689*	828
17	745*	890
23	596*	-962
	3,-5,L	
-15	1521	-1385
-13	1622	-1555
-9	602*	638
-7	733	635
-3	536*	-463
-1	1148	-1246
1	2863	-2894
3	2585	-2265
7	1766	1351
19	819	-919
	3,-4,L	
-13	1225	1092
-11	1008	1149
-7	995	-828
-5	625*	-632
-3	1386	-1251
-1	1286	-1326
1	358*	-445
3	698	693
5	757	723
7	1113	1021
13	925	-899
15	945	-938
	3,-3,L	
-9	1671	-1468
-3	423*	338
3	740	682
5	965	903
9	1198	-1127
11	1892	-1637
13	1875	-1686
	3,-2,L	
-11	1628	-1544
-9	511*	-565
5	469*	-744
7	1871	-951
9	1105	-965
11	759*	720
13	2570	2225
15	1846	1661
	3,-1,L	
-9	1426	1382
-7	1987	2256
7	1062	846
9	2195	1932
11	1932	1681
13	1354	1137
17	720*	-942
	3,0,L	
-9	2039	1807
7	1838	1508
11	1400	-1143
13	2020	-1738
15	1286	-1445
	3,1,L	
-9	2049	-1852
-7	3465	-3336
9	1633	-1386
11	1146	-1116
13	722*	-718
19	732*	941
	3,2,L	
23	604*	-916
	3,3,L	
-3	587	703
5	1201	-943
9	1118	984
11	874	983
17	1091	-1235
19	1516	-1638
	3,4,L	
-5	1099	-1080
1	912	-696
3	3467	2543
5	3514	2732
7	2279	1889
21	857*	1257
	3,5,L	
-7	1359	1082
1	1822	1621
3	3533	2639
9	1754	-1555
11	699*	-672
17	1210	1340
19	1046	1343
	3,6,L	
-9	940	-900
-5	839*	949
-3	983	874
-1	523*	308
1	515*	-378
3	2488	-2251
5	3178	-2599
17	691*	937
	3,7,L	
-7	1075	919
-5	942	953
-1	1507	-1271
1	2224	-2189
3	2213	-1930
7	1472	1322
9	1627	1557
11	1088	1112
19	758*	-1128
	3,8,L	
-7	1080	-993
-5	1538	-1520
-3	1821	-1548
1	1572	1303
7	690*	-650
15	718*	-907
	3,9,L	
-9	1206	-1153
-7	1247	-1241
-3	599*	517
-1	908	848
1	1108	1008
3	920	888
7	758*	-875
9	1448	-1408
11	745*	-898
15	795*	1171
	3,10,L	
-7	1584	1515
-5	2412	1995
-3	1393	1223
3	1256	1120
11	721*	813
13	1712	1756
15	900*	1325
	3,11,L	
-9	743*	963
-7	1212	1234
-3	707*	-664
-1	1131	-1053
3	668*	-817
9	1356	1381
11	879*	1041
15	1129	-1439
	3,12,L	
-7	1050	-1096
-5	1692	-1593
-3	785*	-909
13	704*	-1022
	3,13,L	
-9	877*	-1239
-7	1596	-1625
-5	930*	-1002
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1	1508	1446
5	966	-1018
7	1589	-1645
9	987	-1191
	3,14,L	
3	741*	-749
5	1007	-1129
7	720*	-784
	3,15,L	
-3	697*	-860
-1	703*	-876
5	1030	1198
7	920*	1203
	3,16,L	
3	917*	1128
5	887*	1158
	3,17,L	
-1	705*	781
5	815*	-995
7	774*	-1129
	3,18,L	
-3	650*	528
3	776*	-1077
5	920*	-1244
	4,-17,L	
-2	1274	-950
0	1065	-815
2	1078	-740
	4,-16,L	
-8	1230	-1145
-6	1012	-895
-4	569*	-642
14	601	-825
	4,-15,L	
-2	774	820
0	1147	1207
2	711	774
6	600*	-761
8	854	-1078
	4,-14,L	
-12	571*	-558
-8	537*	828
-6	835	813
-4	603*	698
4	1544	-1559
6	953	-1039
10	984	1084
12	993	1146
	4,-13,L	
-10	928	1092
-8	1070	1165
-2	606*	-718
6	1414	1484
8	1441	1460
10	871	968
	4,-12,L	
-14	1051	878
-12	840	903
-8	1374	-1280
-6	1248	-1084
-4	457*	-207
-2	498*	625
0	938	1016
4	634	737
6	575*	705
10	1009	-1052
12	735	-774
	4,-11,L	
-10	1706	-1973
-8	2180	-1947
-4	1185	1158
2	536*	-724
4	433*	-465
6	1103	-1155
8	1043	-1205
10	677	-807
12	672	-233
	4,-10,L	
-16	823	-908
-14	922	-1025
-12	883	-1007
-8	1018	975
-6	1309	1251
-4	531*	586
0	510*	-577
2	1146	-1085
6	618	-758
10	858	906
12	681	782
14	589*	774
18	450*	-527
20	647	-855
	4,-9,L	
-14	919	1039
-12	951	914
-10	883	890
-8	931	912
-4	653	-637
-2	701	-714
0	841	-809
2	478*	-422
4	510*	474
6	1114	1099
8	713	835
14	798	-876
16	1268	-1267
18	765	-847
	4,-8,L	
-18	1544	1218
-16	869	1069
-14	946	887
-6	658	-647
-4	819	-833
-2	984	-828
0	930	849
2	1539	1593
4	1362	1257
6	579	584
8	495*	-563
10	923	-835
12	669	-704
16	539*	541
18	984	1061
20	991	1152
	4,-7,L	
-18	1597	1265
-12	477*	-731
-6	362*	-442
-4	603	649
-2	1865	2009
0	2484	2352
2	1232	1178
6	692	-748
14	672	757
16	1825	1830
18	949	1037
22	555	-735
	4,-6,L	
-16	669	-749
-14	1247	-1179
-8	854	848
-6	1536	1540
-4	871	936
0	1691	-1827
2	2520	-2956
4	1236	-1088
6	686	697
8	613	674
18	1235*	-796
20	948	-1094
22	403*	-618
	4,-5,L	
-18	1099	-1204
-12	881	869
-8	521	411
-4	2402	-2113
-2	1422	-2106
0	1239	-1725
4	927	799
6	1524	1220
8	412*	421
14	926	-882
16	896	-883
18	593*	-632
22	688	765
	4,-4,L	
-16	929	1093
-14	1332	1275
-12	658	648
-10	411*	-525
-8	1190	-1191
-6	1034	-1701
-4	571	-428
-2	771	689
0	821	867
2	1103	1551
6	362*	461
8	449*	-397
10	437*	-456
12	1301	-1179
14	734	-826
20	690	875
22	645	485
	4,-3,L	
-12	867	-910
-10	671	-691
-6	356*	353
-4	1081	1044
-2	950	1190
6	1531	-1513
8	2615	-2409
10	959	-840
12	552*	544
14	1522	1297
16	833	851
22	594	-824
24	456*	-827
	4,-2,L	
-16	826	-1120
-14	573*	-661
-10	1201	1071
-8	2329	2147
-6	1025	952
8	1243	1116
10	2185	1798
12	2127	1685
14	516*	583
	4,-1,L	
-12	1003	962
-10	1820	1506
-8	1521	1376
-2	758	-1231
2	174*	-228
6	3025	2457
8	3218	2642
10	463*	-416
12	2016	-1666
14	1727	-1533
18	550*	427
	4,0,L	
-10	1041	-930
-8	1894	-1889
-6	2479	-2753
6	482	330
8	1202	-1044
10	2897	-2310
12	1565	-1394
22	778	894
	4,1,L	
-8	1469	-1493
6	1801	-1347
8	822	-701
12	1154	1063
14	962	996
24	556	-835
	4,2,L	
2	471	-449
6	997	-893
12	508*	501
14	676	669
18	1237	-1296
20	1163	-1252
22	726	-858
	4,3,L	
-6	512*	-830
2	2158	1595

* These reflections were treated as unobserveds.

TABLE 3.7 page 5

4,3,L

4	2997	2212
6	987	791
8	717*	701
20	497*	624
22	439*	680

4,4,L

0	2185	1770
2	2887	2330
4	2232	1749
6	1034	903
10	760	-749
12	934	-899
16	1077	1132
18	2036	2042
20	992	1264

4,5,L

-4	1504	1287
-2	1932	1719
0	978	712
2	967	-832
4	3003	-2620
6	385*	-474
16	597*	694
20	481*	-661

4,6,L

-4	840	843
-2	316*	-285
0	2292	-1704
2	2551	-2140
4	2159	-1829
8	661	663
10	1401	1347
12	906	1011
16	808	-856
18	1415	-1617
20	490*	-710

4,7,L

-6	1038	-1042
-4	2201	-1991
-2	1895	-1752
0	511	-497
2	2061	1863
4	1950	1711
6	376*	421
8	563*	-394
10	423*	-412
14	550*	-691
16	898	-1143
18	534*	-791

4,8,L

-6	1057	-1182
-4	765	-715
0	1320	1106
2	1834	1592
4	809	760
6	962	-939
8	1522	-1471
10	1862	-1881

4,9,L

-6	2064	1943
-4	1614	1495
-2	467*	483
0	663	-689
2	463*	-348
12	1260	1365
14	926	1103
18	518*	765

4,10,L

-8	1242	1371
-6	997	1032
-4	522*	468
2	607	-626
4	996	-1065
8	2099	1977
10	2037	2102
12	818	880
16	853	-997

4,11,L

-8	843	-928
-6	1337	-1232
-4	675	-811
2	1028	-978
4	533*	-440
6	760	809
8	1333	1309
12	919	-1175
14	880	-1077
16	501*	-813

4,12,L

-8	1318	-1564
-6	1151	-1193
0	786	925
2	848	888
6	707	-674
8	1738	-1696
10	1175	-1275
14	709	912

4,13,L

-4	841	874
2	559*	-614
4	881	-889
6	822	-899
8	589*	-810

4,14,L

-6	1039	1181
-2	753	-871
0	1686	-1570
2	1179	-1088
6	542*	745
8	553	720

4,15,L

2	902	965
4	831	884
6	463*	737
8	552	788
14	483*	-783
10	639	769

4,16,L

-2	907	995
0	1049	1174

4,17,L

2	703	-810
4	713	-842

4,18,L

0	484*	-864

4,19,L

4	825	986

5,-16,L

-3	380*	458
-1	543	618
1	447	481
9	495	-558

5,-15,L

-7	850	695
-5	878	931
-3	305*	479
3	585	-681
5	803	-875
7	439	-500
11	819	807
13	818	790
15	234*	145

5,-14,L

-7	381*	435
-3	530	-518
-1	1183	-1148
1	522	-747
3	553	-740
5	531	526
7	1205	1215
9	1168	1169
13	378*	-534

5,-13,L

-11	512	463
-7	319*	-487
-3	436	-468
-1	326*	-400
1	640	656
3	1299	1301
5	2330	2264
7	570	756
9	551	-626
11	1009	-951
13	379*	-424
15	296*	348
17	291*	377

5,-12,L

-11	1128	-1227
-9	1078	-1238
-5	721	689
-3	661	838
5	464	-406
7	1248	-1235
9	966	-1123
11	273*	-296
19	279*	396

5,-11,L

-15	1046	-997
-13	1426	-1391
-11	1148	-1187
-7	922	895
-5	829	730
-1	629	-702
1	1115	-1115
3	1123	-1166
5	1219	-1316
9	445	358
11	681	597
13	526	578

5,-10,L

-15	354*	-395
-13	515	475
-11	1012	1143
-9	1273	1242
-7	371*	445
-5	596	-606
-3	593	-601
-1	507	-536
1	265*	-415
7	729	954
9	779	839
11	750	845
15	844	-881
17	913	-930
19	869	-825

5,-9,L

-15	727	923
-13	655	758
-7	475	-462
-5	1069	-1027
-3	890	-873
1	1370	1227
3	1036	1124
9	714	-686
11	923	-956
13	1133	-1123
15	321*	-416
17	817	640
19	671	624
21	231*	425

5,-8,L

-15	296*	-370
-13	982	-1072
-3	379	383
-1	1673	1668
1	1400	1239
7	242*	-320
9	602	-638
11	391	-403
13	480	531
15	1536	1707
17	1790	1631
19	468	470

5,-7,L

-15	415	-609
-13	546	-734
-7	1047	1012
-5	2011	1968
-3	1589	1748
-1	425	289
1	1381	-1593
3	1627	-1611
7	573	474
9	694	762
11	829	867
13	647	629
15	530	518
17	519	-443
19	844	-847

5,-6,L

-13	497	606
-7	413	416
-3	1442	-1498
5	298*	384
9	561	544
11	398	339
13	971	-877
15	1636	-1492
17	1331	-1358
19	256*	-195
21	495	539

5,-5,L

-15	506	764
-13	1348	1350
-9	1200	-1087
-7	1894	-1946
-5	1746	-1934
-3	722	-796
-1	688	900
5	565	-542
7	982	-906
9	331*	-343
13	753	-729
15	712	-607
19	711	756
21	781	633

5,-4,L

-11	996	-985
-9	499	-541
-7	574	-536
-5	304	346
-3	1316	1327
7	1306	-1457
9	1408	-1193
11	404	-349
13	666	582
15	711	721
17	706	730
21	696	-663
23	822	-963

5,-3,L

-15	1136	-1206
-11	418	269
-9	1840	1831
-7	1700	1719
-3	284	-261
5	458	-600
9	719	528
11	793	859
13	1017	1019
15	556	523
17	293*	244
19	387	-530
23	792	-351
21	819	-822

5,-2,L

-13	490	644
-11	1165	1104
-9	694	599
-7	438	428
-3	370	375
7	2669	3048
9	1963	2279
13	1155	-997
15	549	-562
21	583	516
23	413	1013

5,-1,L

-9	1676	-1547
-7	1532	-1523
-3	360	471
1	246	-323
5	1011	874
9	2016	-1578
11	1786	-1418
13	692	-565
19	338*	323
21	704	822
23	373	436

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-9	2238	-1919
-7	1268	-1294
-5	414	-452
5	1051	-2891
7	2893	-2818
9	1230	-1003
11	1193	1113
13	1384	1271
15	485	578
17	352*	-241
23	474	-533

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1	190	-146
5	878	-783
9	746	648
11	1029	907
13	752	789
15	512	544
17	353*	-466
19	1174	-1215
21	987	-1155
23	631	-801

5,2,L

1	275	-224
3	962	945
5	874	721
7	467	447
11	564	-348
13	986	-861
15	805	-841
17	502	-571
19	525	-436
23	432	496

5,3,L

1	1422	1263
3	1693	1124
5	372	242
7	794	697
9	717	526
11	1009	-909
13	1186	-1064
17	1491	1479
19	1684	1601
21	788	911

5,4,L

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-3	2100	2429
-1	2472	2215
3	1057	-924
5	1063	-847
13	1132	1068
15	1239	1188
17	899	695
21	415	-436

5,5,L

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1	1140	-1180
3	1727	-1405
5	1165	-1029
7	962	-954
11	1159	1096
13	1423	1351
15	346*	-298
17	1512	-1493
19	1292	-1367

5,6,L

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-3	2445	-2405
-1	1294	-1102
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3	1181	1136
5	1359	1086
13	438	-364
15	926	-967
17	591	-693
21	280*	479

5,7,L

-7	605	-727
-5	1162	-1084
-3	647	-622
-1	598	485
1	1617	1491
3	1694	1571

* These reflections were treated as unobserveds

TABLE 3.7 page 6

	5,7,L	
5	402	315
7	1262	-1013
9	1022	-965
11	1380	-1405
13	664	-777
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19	485	709
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1	1034	-861
3	957	-848
5	1310	-1211
13	302*	315
17	300*	585
19	544	581
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1	676	-665
3	297*	-397
5	253*	254
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9	1399	1305
11	905	1044
13	583	477
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5	713	810
7	1544	1476
11	618	-615
13	558	-790
15	448	-644
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-3	509	-528
1	336*	397
3	1473	1371
5	865	646
7	1180	-1160
9	1870	-1840
11	1084	-1275
15	271*	464
17	302*	560
19	300	559
	5,12,L	
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-5	718	685
1	426	-247
5	859	-857
7	1070	-1130
9	290*	226
11	518	598
13	404	577
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1	1424	-1466
3	938	-970
7	994	1048
9	598	773
15	324*	-560
17	385	-575
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3	917	942
5	1220	1178
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13	255*	-499
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3	281*	440
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1	681	-716
3	719	-861
7	367	-500
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5	433	553
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8	574	609
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2	1024	959
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8	942	-883
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-12	860	-965
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4	1694	-1869
6	1257	-1349
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-2	683	-689
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2	421*	-550
4	392	-462
6	517	510
8	884	924
10	430*	579
16	273*	-400
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-10	770	714
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4	518	770
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8	991	-900
10	949	-812
12	766	-652
14	491	506
16	1349	1351
18	893	867
20	270*	357
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14	963	992
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18	831	-719
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-8	1043	-955
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0	860	1080
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8	1068	-1243
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14	740	703
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6	339	290
14	518	515
20	904	-856
22	789	-795
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8	1226	1821
10	601	557
12	351*	362
16	401*	-468
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-2	371	407
6	621	571
8	427	-420
10	667	-560
12	368	-394
14	420	-453
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22	825	1047
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22	645	-599
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20	745	-737
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12	1343	-1172
14	459	-535
16	733	-696
18	794	-738
20	416	-471
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14	1312	1207
16	1502	1301
18	759	647
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6	773	-626
8	658	-471
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12	1557	1629
14	518	488
16	888	-761
18	1257	-1391
20	671	-700
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20	344*	371
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16	654	650
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-2	1537	1735
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2	427	-297
4	905	-976
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8	709	-647
10	663	-629
12	387*	398
14	607	614
20	283*	-498
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4	458	-415
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8	1131	1179
10	1047	950
12	671	713
14	312*	586
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6	1378	1487
8	903	651
12	318*	-311
18	369	-493
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2	1042	811
4	948	783
8	831	-969
10	1015	-1007
12	1023	-1 43
18	309*	417
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0	445*	449
4	1248	-1072
6	1665	-1714
8	1195	-956
12	296*	468

* These reflections were treated as unobserveds

6,11,L		
14	707	766
16	455	643
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4	370*	-561
8	722	673
10	592	653
14	266*	-190
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0	551	-470
4	783	746
6	836	964
8	331*	384
10	291*	-483
12	606	-538
14	590	-682
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0	1370	1187
2	1081	1056
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2	521	-574
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12	441	550
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8	274*	-182
10	253*	503
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7,-13,L		
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-1	1068	993
3	2011	-1421
5	2378	-1574
7,-12,L		
-1	1370	-1173
1	1516	-1356
7,-11,L		
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-3	1192	-1028
3	1430	1373
5	1203	1229
7,-10,L		
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-5	834*	869
9	761*	-883
7,-9,L		
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-5	1800	1802
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11	1100	1172
13	1263	1214
7,-8,L		
7	700*	565
9	1632	1710
11	1398	1359
15	1016	-1060
7,-7,L		
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-3	1566	-1624
9	729*	-716
11	1582	-1448
13	1157	-1239
7,-6,L		
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-5	804	-761
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1	829	871
5	670*	-674
7	759	-905
9	1863	-1907
13	775*	814
15	986*	1129
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-7	1039	1086
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-1	509*	-719
1	1033	-1296
3	640*	-619
11	1296	1279
13	815*	902
7,-4,L		
-11	1118	1230
-7	747*	839
1	669	-815
17	771*	-911
7,-3,L		
-9	839*	-898
-5	792	-827
-1	507*	572
5	737*	736
19	749*	912
7,-2,L		
5	1150	-1466
7	1682	-1776
19	793*	410
21	1020	-515
7,-1,L		
5	1344	-1554
19	640*	-747
7,0,L		
5	1407	1343
7	1302	1086
19	640*	-610
7,1,L		
1	1028	1037
3	1084	890
5	674*	746
11	697*	-859
13	857*	-902
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15	806*	871
17	937*	1166
7,3,L		
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11	1333	1315
13	1304	1221
7,4,L		
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-3	1362	-1303
-1	487*	-748
13	774*	-982
15	1389	-1385
17	747*	-901
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-5	1059	-1212
11	1516	-1706
13	992*	-1094
17	698*	704
7,6,L		
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-1	1092	1015
7	870*	-967
15	783*	1060
7,7,L		
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-1	965	-983
1	1266	-1228
3	696*	-978
7,8,L		
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3	681*	866
5	1382	1476
7	1284	1399
7,9,L		
1	808*	984
7,10,L		
-1	777*	994
5	1690	-1637
7	1542	-1578
7,11,L		
1	921*	-1050
7,12,L		
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7	765*	936
7,14,L		
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-3	1130	1465
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11	668	873
7,16,L		
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8,-11,L		
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8,-10,L		
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6	997	-917
14	657*	612
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8	1217	1159
10	917	1072
12	781*	917
8,-8,L		
-10	617*	741
-6	1584	-1271
-4	625*	-722
6	806*	905
10	756*	-925
14	677*	-755
8,-7,L		
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-6	618*	-745
6	664*	-528
8	1844	-1578
10	1606	-1673
8,-6,L		
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-10	774*	-877
-6	1453	1318
-4	1323	1312
2	643*	-896
4	969	-938
6	843	-708
10	913	973
12	669*	965
8,-5,L		
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-8	1131	1239
-6	517*	659
-2	770	-812
0	865	-908
6	1022	949
8	896	865
8,-4,L		
-12	737*	922
-6	889	-1077
-4	948	-909
4	558*	687
6	567*	787
16	605*	-474
8,-3,L		
-10	629*	-826
-4	680*	546
-2	1029	1086
8,-2,L		
-6	671*	829
-4	894	864
4	1424	-1485
6	525*	-518
18	1446	-729
8,-1,L		
6	1101	982
18	1253	-700
8,0,L		
4	1487	1753
6	1016	753
10	968*	-739
12	673*	-834
18	845*	515
8,1,L		
6	626*	-638
8	837	-691
10	602*	-627
18	598*	713
8,2,L		
2	1011	-1021
10	1458	1357
12	1366	1384
8,3,L		
8	1013	1028
10	1083	1058
16	581*	-816
8,4,L		
-6	1034	-1666
10	1519	-1449
12	1412	-1407
8,5,L		
8	1391	-1531
10	1255	-1287
14	1179	1245
16	645*	966
8,6,L		
10	784*	1024
8,7,L		
8	1330	978
8,8,L		
0	826*	1617
2	755*	1274
8,9,L		
-2	627*	953
4	951	-744
6	671*	-1298
14	859	413

* These reflections were treated as unobserveds.

CHAPTER 4

Reactions of Platinum(II) NN-Dialkyl Dithiocarbamates, O-Ethyl Dithiocarbonate (Xanthate) and OO'-Diethyl Dithiophosphate

CHAPTER 4

Reactions of Platinum (II) NN-Dialkyl Dithiocarbamates, O-Ethyl Dithiocarbonate (Xanthate) and OO'-Diethyl Dithiophosphate with tertiary phosphines.

4.1 Introduction

As described earlier (Chapters 2 and 3) the reaction of tertiary phosphines with bis(diphenylphosphinodithioato)palladium (II) or platinum(II) produced stepwise cleavage of the metal-sulphur bonds of one of the bidentate ligands, generating the four-coordinate complexes $M(S_2PPh_2)_2PR_3$ and $[M(S_2PPh_2)(PR_3)_2]S_2PPh_2$ (M=Pd, Pt; PR_3=tertiary phosphine).

However, an earlier report of the reactions of PPh_2Me with $M(S\text{-}S)_2$ (1:1 molar ratios) (M=Pd, Pt; $(S\text{-}S)^- = {}^-S_2CNEt_2$, ${}^-S_2COR$, ${}^-S_2P(OEt)_2$ and ${}^-S_2CR$) formulated the products $M(S\text{-}S)_2PPh_2Me$ as five-coordinate complexes [50, 51] and the addition of excess PPh_2Me to platinum (II) ring-substituted dithiobenzoates precipitated complexes which were tentatively assigned six-coordinate structures [50, 51]. Excess $PMePh_2$ was reported to react only slowly with diethyldithiocarbamate complexes of platinum (II) and palladium (II) and no solid products were isolated. The products in solution were incompletely characterised but were thought to contain tertiary phosphine coordinated to the metal [50]. Furthermore, the addition of excess tertiary phosphine to palladium and platinum xanthate and dithiophosphate was found to give the novel complexes $(R_3P)_2MS_2CO$ and $(R_3P)_2PdS_2P(O)OEt$ respectively for which no

convincing reaction mechanism was suggested [40].

Therefore, it was of considerable interest to determine whether the $^{-}S_2PR_2$ (R=Me [51], Et [61], Ph, F [60]) complexes of palladium and platinum (II) do exhibit a different type of behaviour with tertiary phosphines from those of other palladium and platinum (II) dithiolates. Hence, in this chapter, the results of a re-examination and extension of the reactions of other $M(S\text{-}S)_2$ compounds with tertiary phosphines are presented and discussed.

4.2 Preparation of the complexes $M(S\text{-}S)_2$

Yellow complexes of the type $M(S\text{-}S)_2$ (M=Pd, Pt; $(S\text{-}S)^{-}$ = $^{-}S_2CNEt_2$ [33], $^{-}S_2CNMe_2$ [33], $^{-}S_2P(OEt)_2$ [33], $^{-}S_2COEt$ [75]) were prepared by treating potassium tetrachloroplatinate (II) or palladium (II) acetate with an ionic salt of the dithio-acid. X-ray studies and magnetic susceptibility measurements have shown that the complexes were square planar chelate monomers [5]. Unlike the complexes of diphenylphosphinodithioic acid, changes in the dithio-ligands in these complexes during the course of reactions could be readily monitored by ^{1}H n.m.r. spectroscopy, although the complexes of the type $M(S\text{-}S)_2$ tended to have poor solubility in most solvents.

4.3 Reaction of $M(S\text{-}S)_2$ with tertiary phosphines (1:1 molar ratios)

Reaction of $Pt(S_2CNEt_2)_2$ with either PPh_3 or $PMePh_2$ (1:1 molar ratios) in carbon disulphide gave immediate deep lemon-yellow solutions from which crystalline yellow solids of stoicheiometry $Pt(S_2CNEt_2)_2PR_3$ were isolated by partial removal of the solvent, followed by cooling. This was in contrast to earlier work [50, 51] where

no pure solid products were isolated from the reaction with $PMePh_2$. The products were non-conducting, diamagnetic and quite stable in both solid and solution state. Similar reactions were observed to occur when other tertiary phosphines, or triphenylarsine were used, but attempted isolation gave mixtures of the 1:1 complex and $Pt(S_2CNEt_2)_2$. Preparation of the PMe_2Ph complex was complicated by the side-reaction between carbon disulphide and the phosphine, which gave the red adduct $PMe_2Ph.CS_2$[76].

$Pt(S_2CNMe_2)_2$ also reacted with $PMePh_2$ in carbon disulphide, and although a pure solid product was not obtained, ^1H n.m.r. studies of the reaction mixture showed the formation of a similar 1:1 complex *in situ*. Addition of triphenylphosphine to $Pd(S_2CNMe_2)_2$ in carbon disulphide produced a yellow solution, suggesting that some formation of the $M(S\text{-}S)_2PR_3$ species occurred, but no pure products were obtainable.

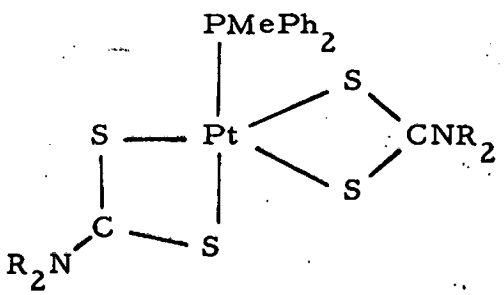
When $Pt[S_2P(OEt)_2]_2$ was shaken with triphenylphosphine (1:1 molar ratios) in dichloromethane solution a yellow solution was obtained from which yellow crystals of $Pt[S_2P(OEt)_2]_2PPh_3$ were obtained by slow evaporation of the solvent in the presence of an excess of light petroleum. Solution i.r. and ^1H n.m.r. spectra indicated that a similar product was formed *in situ* by the reaction of excess triphenylarsine with $Pt[S_2P(OEt)_2]_2$.

The corresponding xanthate complex $Pt(S_2COEt)_2PPh_3$ was also prepared by the reaction of 1:1 molar ratios of $Pt(S_2COEt)_2$ and triphenylphosphine in chloroform, followed by trituration with an

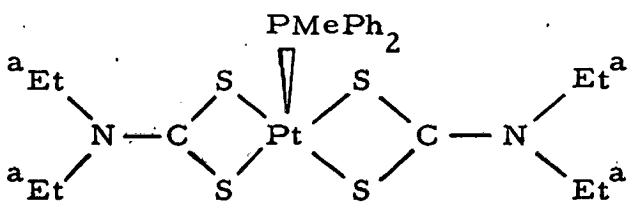
excess of light petroleum, giving a pale yellow crystalline product.

At 301 K, the ^{1}H n.m.r. spectra of the complexes described above were found to be closely similar to those previously reported for the complexes $M(S\text{-}S)_2PMePh_2$ prepared *in situ* (M=Pd, Pt; S-S$^-$ = $^-S_2CNEt_2$, $^-S_2COEt$, $^-S_2P(OEt)_2$, ^-S_2CR) [50, 51] (Table 4.1). Tertiary phosphine coordination, in the case of the dimethylphenyl- or methyldiphenyl-phosphine was indicated by the doublet near τ8.00 ($J_{P\text{-}H} \simeq 10$ Hz) [56], and coordination of the phosphine to the metal atom was confirmed in the platinum complexes by the smaller doublet of doublets in this region ($J_{Pt^{195} - H} \simeq 34\text{-}38$ Hz) [50, 56].

Variable temperature ^{1}H n.m.r. studies of $Pt[S_2P(OEt)_2]_2PMePh_2$ had shown the presence of two magnetically non-equivalent ethyl groups at low temperature [51], whereas the ^{1}H n.m.r. behaviour of $Pt(S_2CNEt_2)_2PMePh_2$ was reported to be essentially independant of temperature from room temperature to -70°C in carbon disulphide [51]. These results had been interpreted in terms of an equilibrium at room temperature between a trigonal bipyramidal (1) and a square pyramidal (2) five coordinate structure, with the latter as the preferred low temperature form.



(1)



(2)

TABLE 4.1

^{1}H n.m.r. data for dithiocarbamate, xanthate and dithiophosphate 1:1 complexes

Compound	Solvent	T(K)	τ Value[a] Dithio-ligand CH_3[f]	Dithio-ligand CH_2[g]	$CH_3(PR'_3)$[b]	Phenyl[c]	J(P-H)[d]	J(Pt-H)[e]
$Pt(S_2CNEt_2)_2$	$CDCl_3$	301	8.70(3)[h]	6.40(2)	-	-		
$Pt(S_2CNEt_2)_2PPh_3$	$CDCl_3$-	301	8.89(12)	6.33(8)	-			
	CS_2					2.2-2.8(15)		
		203	8.96(6);8.88(6)	6.45(4);6.20(4)	-			
$Pt(S_2CNEt_2)_2PMePh_2$	$CDCl_3$	301	8.80(12)	6.26(8)	-			
					7.72(3)	2.2-2.6(10)	10.0	38.0
		213	8.82(6);8.76(6)	6.37(4);6.17(4)				
$Pt(S_2CNMe_2)PMePh_2$	$CDCl_3$-	301	6.64(12) (s)	-				
	CS_2				7.69(3)	2.6(10)	10.7	35.0
		193	6.81(6) (s);6.46(6) (s)	-				
$Pt\left[(S_2P(OEt)_2\right]_2PPh_3$	$CDCl_3$	301	8.70(12)	5.90(8)[i]				
					-	2.6(15)		
		213	8.74(6);8.66(6)	5.90(8)[i]				

Table 4.1 page 2

Compound	Solvent	T(K)	↑ Value[a] Dithio-ligand CH_3[f]	Dithio-ligand CH_2[g]	$CH_3(PR'_3)$[b]	Phenyl[c]	J(P-H)[d]	J(Pt-H)[e]
$Pt[S_2P(OEt)_2]_2AsPh_3$[j]	$CDCl_3$	301	8.69(12)	6.00(8)[i]	-	k		
		223	8.71(6);8.62(6)	6.00(8)[i]				
$Pt(S_2COEt)_2PPh_3$	$CDCl_3$	301	8.62(6)	5.46(4)		2.5(15)		
	CS_2	183	8.62(6) (s) (br)	5.46(4) (s) (br)				

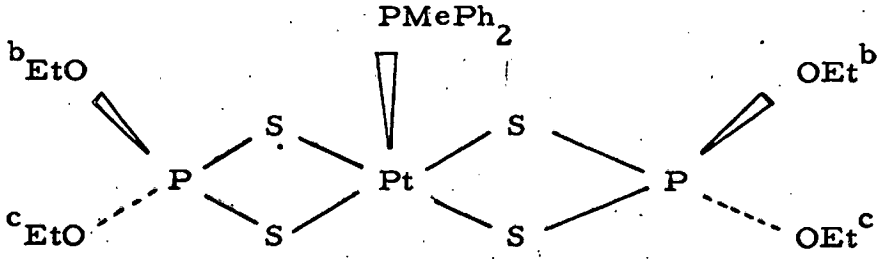
(s) singlet; (d) doublet; (br) broad

a ±0.01. b Triplet of doublets unless otherwise stated. c Phenyl resonance; complex multiplet. d ±0.2Hz.

e ±0.5Hz. f Triplet unless otherwise stated ($J_{CH_2CH_3}$ 7.0Hz). g Quartet unless otherwise stated ($J_{CH_2CH_3}$ 7.0Hz).

h Numbers in parentheses indicate normalised integrated intensities. i Complex multiplet. j $Pt[S_2P(OEt)_2]_2$ + excess $AsPh_3$ in situ. k Not recorded since an excess of $AsPh_3$ present.

In the square pyramidal structure (2), the geometry of the $S_2C{=}N$ group of the dithiocarbamate ligand causes all the ethyl groups to lie in the plane of the chelate ring thus making them all magnetically equivalent, but in the dithiophosphate square pyramidal complex (3), the ethoxy groups lie



(3)

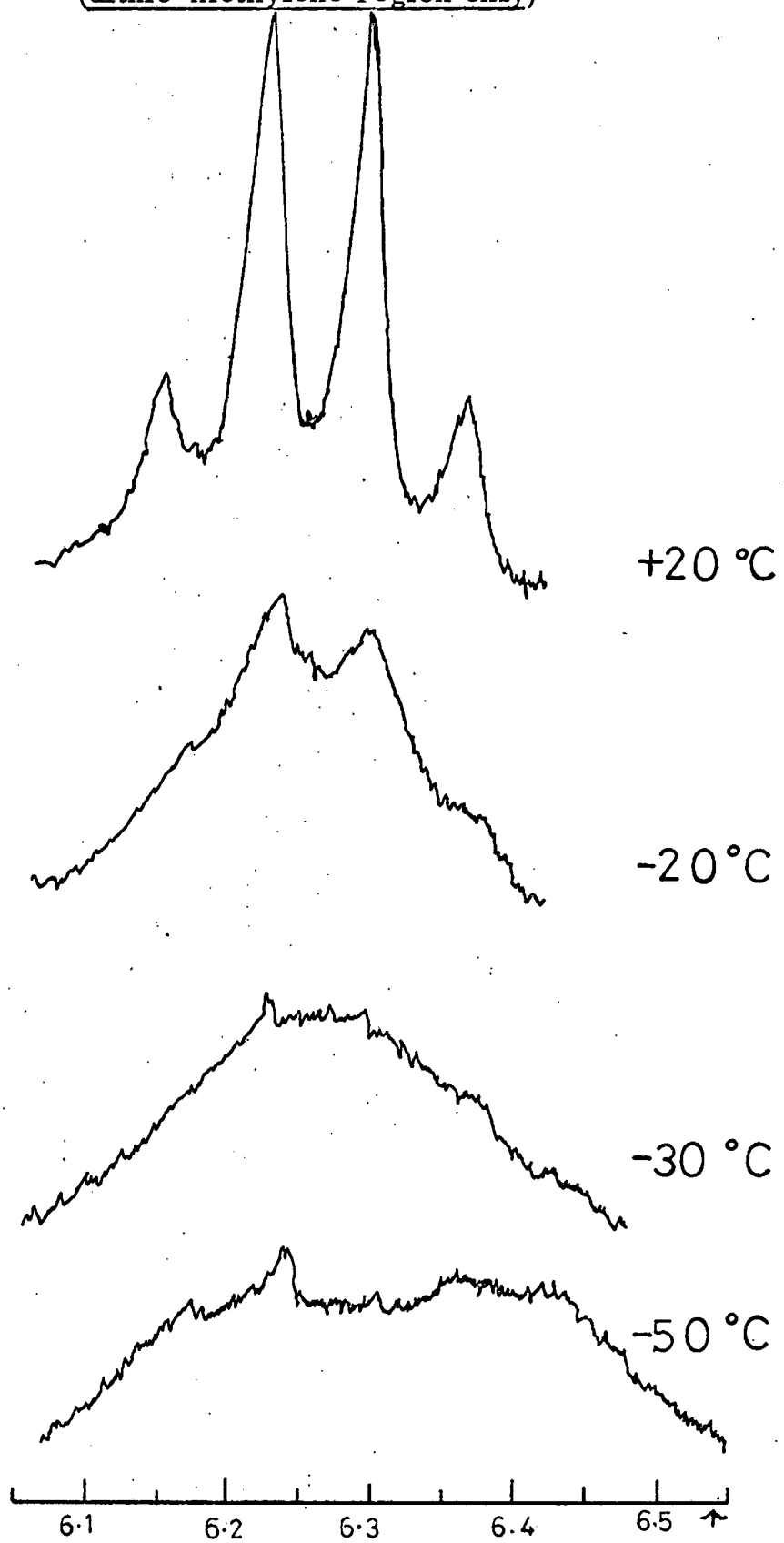
above and below the plane of the chelate ring (in a plane almost perpendicular to the MS_4 plane) forming two magnetically non-equivalent groups.

However, our studies of the variable temperature ^1H n.m.r. behaviour of the dithiocarbamate complexes (using a 100 MHz n.m.r. machine) showed considerable temperature dependance in the spectra obtained (see Table 4.1 and Figures 4.1 and 4.2). For example, the room temperature spectrum of $\underline{Pt(S_2CNEt_2)_2PMePh_2}$ in CS_2 or $CDCl_3$ showed, in the dithio-ligand region, a single triplet at τ8.80 and a quartet at τ6.26 due to the ligand methyl and methylene protons respectively (Figure 4.1). This proved to be a deceptively simple spectrum since on cooling, the CH_2 quartet at τ6.26 started to

FIGURE 4.1

Variable Temperature ^{1}H n.m.r. spectra of $Pt(S_2CNEt_2)_2PPh_2Me$

(dithio-methylene region only)



broaden at ca 253 K, coalesced at ca 240 K, and at 213 K exhibited a limiting spectrum of two broadened signals, with some unresolved fine structure, centred at τ6.37 and 6.17 (separation 20 Hz). Likewise, the single CH_3 triplet resonance (τ8.80) started to broaden at ca 230 K, and at 213 K consisted of an overlapping doublet of triplets centred at τ8.82 and 8.76 (separation 6 Hz). Initially, it was considered that the discrepancy between these observations and those reported earlier by Fackler[51] was due partly to their use of a 60 MHz instrument (compared with the present studies using a 100 MHz instrument) since the limiting methyl separation at ca 213 K would be only 3.6 Hz, and partly due to their failure to look at the temperature dependence of the CH_2 quartet where the limiting separation is greater (estimated 12 Hz at 213 K). However, Fackler and Andrews[77] independently re-examined this system on a 60 MHz n.m.r. machine, and observed the same temperature dependent spectra as reported above, showing the results reported earlier by Fackler[51] were incorrect.

Similarly $Pt(S_2CNEt_2)_2PPh_3$ exhibited a single CH_2 quartet (τ6.33) and CH_3 triplet (τ8.89) in the ^1H n.m.r. spectrum at 301 K. At 203 K two broadened quartets at τ6.45 and 6.20 (separation 25 Hz) and an overlapping doublet of triplets at τ8.96 and 8.88 (separation 8 Hz) were obtained (Figure 4.2).

The complex $Pt(S_2CNMe_2)_2PMePh_2$ (prepared *in situ*), in a mixture of CS_2 and $CDCl_3$ also showed a single dithio-ligand methyl resonance at 301 K (τ6.64) which broadened on cooling, and was split into two equivalent resonances at 193 K at τ6.81 and 6.46 (separation

FIGURE 4.2

Variable Temperature ^{1}H n.m.r. spectra of $Pt(S_2CNEt_2)_2PPh_3$

(dithio-methylene region only)

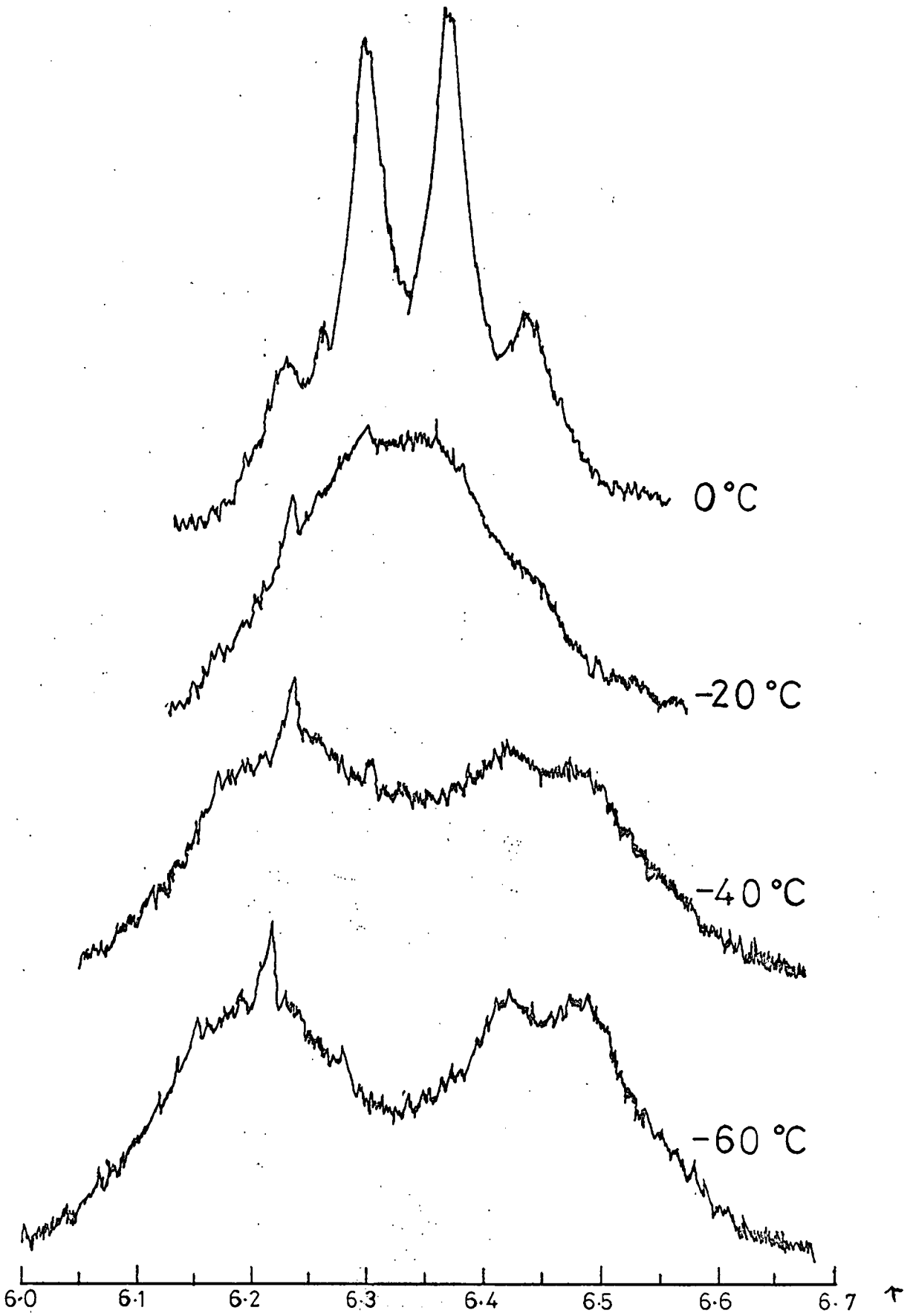
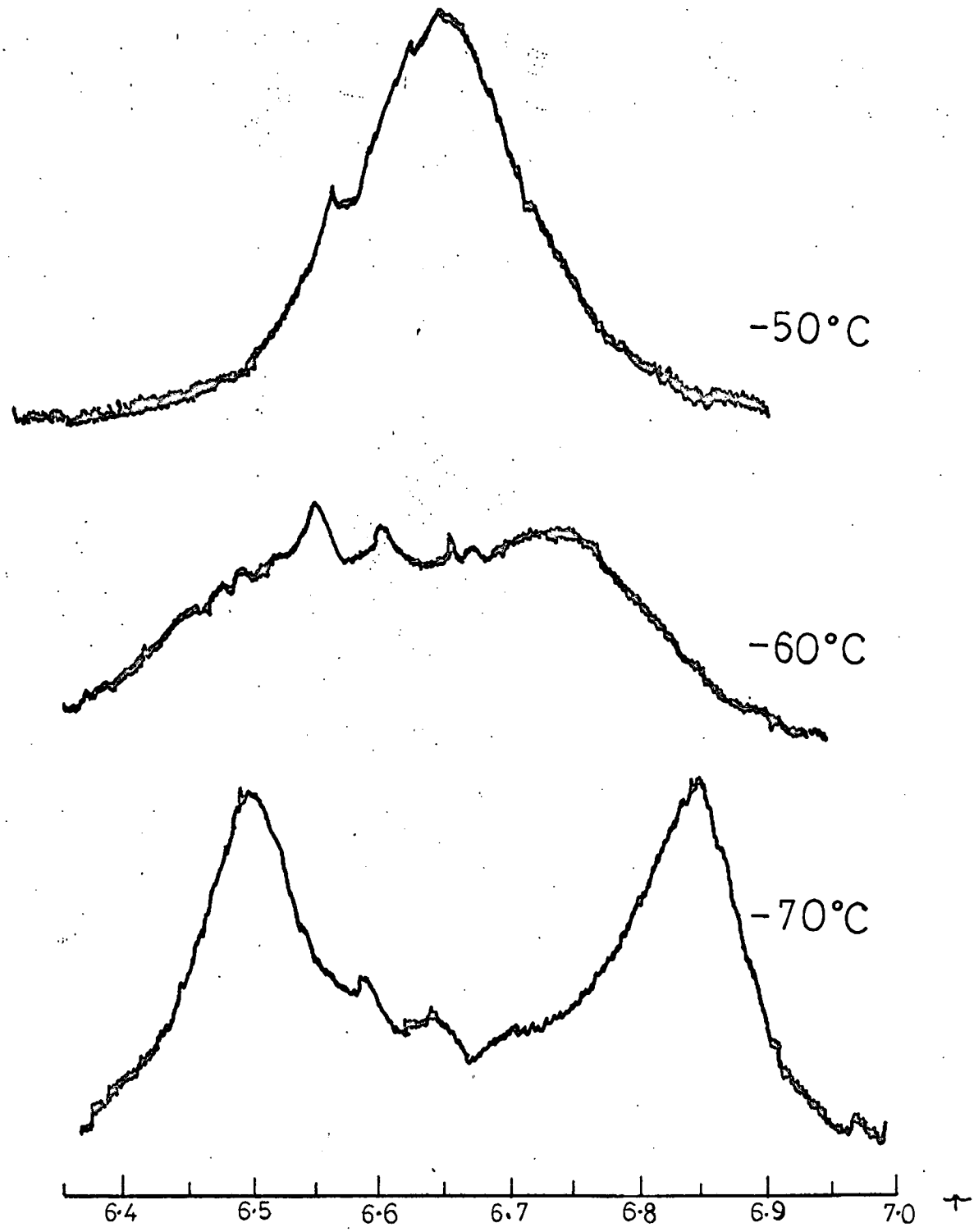


FIGURE 4.3

Variable Temperature ^{1}H n.m.r. spectra of $Pt(S_2CNMe_2)_2PMePh_2$

(dithio-methyl region only)



35 Hz) (Figure 4.3).

The xanthate and dithiophosphate complexes $Pt(S\text{-}S)_2ER_3$ ($S\text{-}S^- = {}^-S_2P(OEt)_2$, $ER_3 = PPh_3$, $AsPh_3$ (in situ); $S\text{-}S^- = {}^-S_2COEt$, $ER_3 = PPh_3$) showed temperature dependent ^1H n.m.r. spectra in $CDCl_3$ or CS_2 solution which were fairly similar to those previously reported for the $PMePh_2$ complexes (Table 4.1). The dithiophosphate complexes with triphenyl-arsine or -phosphine showed single resonances for the CH_2 protons of the dithio-ligand at room temperature. These resonances were complex due to the additional coupling to the ligand phosphorus atoms. At 213 K (223 K for the arsine complex) only the separation of the magnetically non-equivalent methylene protons was observable (see Figure 4.4). The ^1H n.m.r. spectrum of $Pt(S_2COEt)_2PPh_3$ showed broadening of the methylene and methyl proton signals at 183 K, and presumably separation would have occurred had even lower temperatures been obtainable.

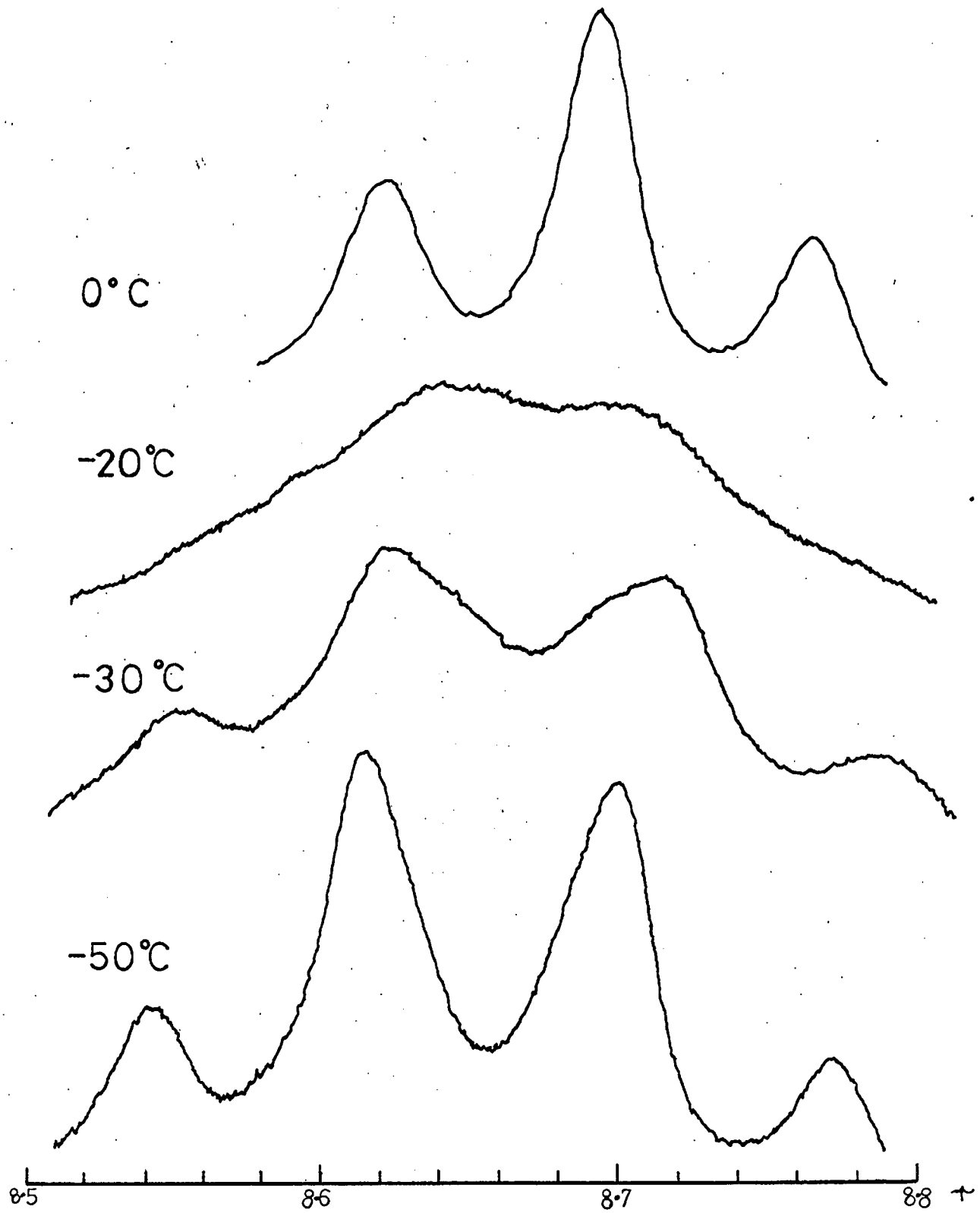
The variable temperature ^1H n.m.r. spectra of $Pt(S_2PMe_2)_2PR_3$ [61] ($PR_3 = PPh_3$, $PMePh_2$) and the variable temperature ^9F n.m.r. spectrum of $Pd(S_2PF_2)_2P(MeC_6H_4)_3$ [60] showed similar behaviour to the above.

In all these cases, the variation of the ^1H n.m.r. spectra with temperature was completely reversible indicating that no gross chemical change occurred. Although the low temperature spectra were not incompatible with a five coordinate trigonal bipyramidal structure of type (1) the observation of magnetically non-equivalent alkyl groups for $Pt(S_2CNR_2)_2PR'_3$ at low temperatures ruled out the

FIGURE 4.4

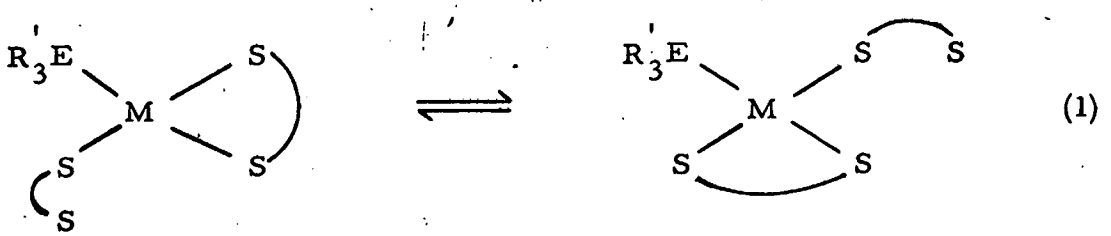
Variable Temperature ^{1}H n.m.r. spectra of $Pt[S_2P(OEt)_2]_2AsPh_3$

(methyl region only)



square pyramidal low temperature structure previously suggested by Fackler[51].

An alternative explanation for the temperature dependent ^1H n.m.r. spectra of all the $M(S\text{-}S)_2ER'_3$ complexes was the presence of an equilibrium between two magnetically equivalent four-coordinate complexes, as indicated in equation (1).



(4) (4) (1)

At higher temperatures rapid interchange of the bidentate and unidentate dithio-ligands produced an averaging of the magnetic nuclei attached to the dithio-ligands, but at low temperatures the intramolecular rearrangement was sufficiently slow for the frozen-out n.m.r. spectrum to be observed.

Several other observations supported this interpretation of the spectra. For example, the chemical shifts and coupling constants for the ^1H n.m.r. phosphine resonances of all the $Pt(S\text{-}S)_2PMePh_2$ complexes at 301 K were closely similar [$(S\text{-}S)^- = {}^-S_2CNR_2$, ${}^-S_2PR_2$[61], ${}^-S_2PPh_2$, ${}^-S_2PF_2$[60], ${}^-S_2P(OEt)_2$, ${}^-S_2COR$], suggesting a similar structure was present in all cases. Also X-ray analyses of $Pd(S_2PPh_2)_2PPh_3$ (Chapter 3) (isomorphous with the corresponding platinum complex), $Pt(S_2CNEt_2)_2PPh_3$ (see Chapter 5) and Pt(p-dithiocumato)$_2$PMePh$_2$[70] have shown that all the structures were

of type (4) in the solid state, and i.r. studies for the S_2PPh_2 complex have indicated that this structure was also present in solution (see Chapter 2). X-ray studies also showed that the metal-sulphur bond trans to the tertiary phosphine group (expected to be long from considerations of the trans effect) was longer than the other three metal-sulphur bonds which provided further support for an equilibrium process involving breakage of this bond.

Calculation of the activation energies for the temperature-dependent reaction of the 1:1 adducts of $^-S_2P(OEt)_2$, $^-S_2PMe_2$, $^-S_2CNR_2$ estimated from the coalescence temperatures by standard methods[78,61] (Table 4.2) gave closely similar values, which supported the existence of a common mechanism to produce averaging of the dithio-ligand resonances. In addition, the close similarity of the activation energies for the varying types of dithio-ligand indicated that the temperature variation observed for the dithiocarbamate complexes could not be attributed to restricted rotation about the C-N bond, although this had been observed in some dithiocarbamate esters[79]. Furthermore, the position of the low field CH_2 quartet (τ6.17) for $Pt(S_2CNEt_2)_2PMePh_2$ was intermediate between that found for the ionic dithiocarbamate (τ5.86 in $[Ph_3(PhCH_2)P]S_2CNEt_2$) and the bidentate dithiocarbamate ligand (τ6.40 in $Pt(S_2CNEt_2)_2$) suggesting that it was probably due to the retention of a unidentate S_2CNEt_2 group in solution.

However, if the frozen-out structure of the dithiocarbamate complexes are considered more closely (5), it can be seen that the

TABLE 4.2

Free-energy of activation and coalescence temperature (Tc/K) obtained from ^{1}H n.m.r. spectra for various dithio-complexes[61].

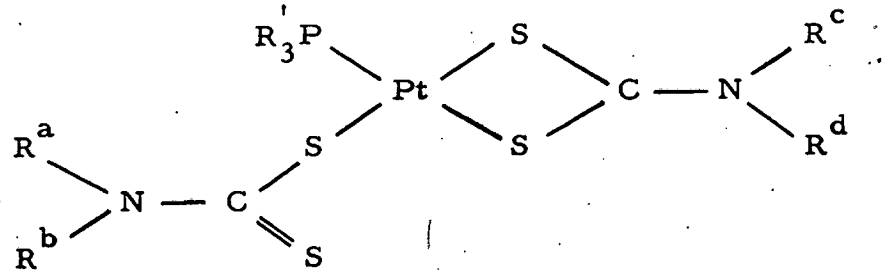
Compound	Tc/K[a]	ΔG^*_{Tc}[b]
$Pt[S_2P(OEt)_2]_2PPh_3$	238[c]	52.3
$Pt(S_2PMe_2)_2PPh_3$	263	55.5
$Pt(S_2CNEt_2)_2PPh_3$	243[d]	5O.8
	233[c]	51.2
$Pt(S_2CNEt_2)_2PMePh_2$	238[d]	5O.2
	228[c]	49.6
$Pt(S_2CNMe_2)_2PMePh_2$	213	43.8
$[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$	253[d]	51.2
$[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$	223	46.5
$CH_2(S_2CNEt_2)_2$	233	65.7[e]
$CH_2(S_2CNMe_2)_2$	243	64.4[f]

[a] $\pm$1K. [b] $\pm$1.0kJ mol^{-1}. [c] Measured on CH_3 triplets.

[d] Measured on CH_2 quartets. [e] Cf. EtS_2CNEt_2 [79] ΔG^*_{298K} 63.8 kJ mol^{-1}.

[f] Cf. MeS_2CNMe_2 [79] ΔG^*_{298K} 61.8 kJ mol^{-1}

observed limiting low temperature ^{1}H n.m.r. spectra are not completely consistent with this structure, since all the alkyl groups should be magnetically non-equivalent.



(5)

Rotation about the Pt-S and C-N bonds of the unidentate dithio-group may be sufficiently rapid to average R^a and R^b, in which case three resonances of intensity ratios 1:1:2 are theoretically expected, whereas only two resonances of equal intensity were observed. However, the atoms S and P inducing the magnetic inequivalence in R^c and R^d are well removed (six bonds) from these groups so that the separation between these resonances may well be too small to be resolved particularly at 213 K where machine line broadening is appreciable. A similar inconsistency has also been found in the square planar complex $[Ni(S_2CNR_2)Cl(PR'_3)]$ where only a single resonance at 213 K was observed and even in $(SiH_3)SOCNMe_2$ where the inequivalence is produced by the greatly differing atoms O and S only four bonds away, the separation of the two methyl groups is only 12 Hz at 301 K[81].

Further support for the existence of four-coordinate 1:1 species of type (4) was the formation of four-coordinate ionic species

$[M(S\text{-}S)(PR_3)_2](S\text{-}S)$ on addition of excess tertiary phosphine to $M(S\text{-}S)_2$ (see section 4.4) which strongly supported a stepwise cleavage of the metal-sulphur bonds of one of the chelate dithio-ligands, producing the 1:1 species as an initial product, similar to those found for the phosphinodithioato-compounds (Chapter 2).

A rapid exchange of the two magnetically equivalent species (4) has also been recently independently suggested by Powell and Chan on the basis of detailed studies of the variable temperature ^1H n.m.r. spectra of the related complexes [π-allylPd(PMe_2Ph)(X-Y)] (X-Y= $^-S_2CNMe_2$, $^-S_2COMe$ [82]). A similar mechanism was also suggested for the interconversion processes in some molybdenum dialkyl-dithiocarbamates [83].

4.4 Reaction of Platinum and Palladium dialkyldithiocarbamates with an excess of tertiary phosphine.

a) Preparation of the complexes $[M(S_2CNR_2)(PR'_3)_2S_2CNR_2$

When a suspension of $Pt(S_2CNR_2)_2$ (R=Me, Et) in acetone was shaken with an excess of $PMePh_2$, an immediate pale yellow solution was formed, from which pale yellow crystals of stoicheiometry $[Pt(S_2CNR_2)(PMePh_2)_2]S_2CNR_2$ were rapidly deposited. Attempts to synthesise the PPh_3 complex proved unsuccessful, probably due to steric factors. The presence of ionic as well as coordinated dithio-carbamate groups was indicated by the presence of additional bands in the i.r. spectra which were also found in the i.r. spectra of the sodium dithiocarbamate salts, compared with those shown for $Pt(S_2CNR_2)_2$.

TABLE 4.3

Equivalent conductivities (298K) in CH_2Cl_2 of some platinum dithiocarbamate, xanthate and dithiophosphate complexes

Compound	Conc. (10^{-4}M)	Λ^a
Ph_4AsCl,HCl	9.8	55.3
Bu_4NClO_4	10.1	22.7
	3.1	32.1
$Pt(S_2CNMe_2)_2$	9.2	3.0
$Pt(S_2CNEt_2)_2$	9.4	0.2
$Pt(S_2CNEt_2)_2PPh_3$	16.5	0.7
$Pt(S_2CNEt_2)_2PMePh_2$	17.3	4.3
$[Pt(S_2CNMe_2)(PPh_3)_2]Cl,H_2O$	12.5	34.2
$[Pt(S_2CNMe_2)(PPh_3)_2]BPh_4$	9.0	40.9
$[Pt(S_2CNMe_2)(PMePh_2)_2]Cl,H_2O$	11.2	36.6
$[Pt(S_2CNMe_2)(PMePh_2)_2]BPh_4$	2.4	50.1
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]Cl,2H_2O$	14.7	38.6
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]BPh_4$	8.8	43.8
$[Pt(S_2CNMe_2)(PEtPh_2)_2]BPh_4$	0.4	36.4
$[Pt(S_2CNEt_2)(PPh_3)_2]Cl,H_2O$	6.9	57.5
$[Pt(S_2CNEt_2)(PPh_3)_2]BPh_4$	2.5	51.6
$[Pt(S_2CNEt_2)(PMePh_2)_2]Cl,H_2O$	6.4	57.5
$[Pt(S_2CNEt_2)(PMePh_2)_2]BPh_4$	10.2	42.2
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]Cl,H_2O$	7.9	50.1
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]BPh_4$	5.9	42.7

Table 4.3 page 2

Compound	Conc. (10^{-4}M)	Λ^a
$[Pt\{S_2P(OEt)_2\}(PPh_3)_2]BPh_4$	9.4	27.7
$[Pt(S_2COEt)(PPh_3)_2]BPh_4$	10.2	21.6
$Pt[S_2P(OEt)_2]_2$ + excess PPh_3	10.0	31.0

[a] In Ω^{-1} cm^2 mol^{-1}

Although the compounds were found to be conducting, accurate conductivity measurements were not obtained since a solution of the complex in dichloromethane (or chloroform, but not $CDCl_3$) rapidly decolourised showing that a further reaction occurred on exposure to these chlorinated solvents (see section 4.4b). However, the dithiocarbamate anion of the complex could readily be replaced by the tetraphenylborate ion by shaking with $NaBPh_4$ in methanol to give $[Pt(S_2CNR_2)(PMePh_2)_2]BPh_4$ which showed typical 1:1 electrolyte behaviour in dichloromethane (Table 4.3), and the i.r. spectra as expected showed absence of the bands attributed to the anionic dithiocarbamate group.

In non-polar solvents, the complex $[Pt(S_2CNR_2)(PMePh_2)_2]S_2CNR_2$ rapidly dissociated to the 1:1 complex and free phosphine (cf. the analogous S_2PPh_2 complexes), and this tendency was enhanced by the greater nucleophilicity of the $^-S_2CNR_2$ ligand compared to $^-S_2PPh_2$ [54]. Thus, although the complex was insoluble in benzene (ε = 2.28), a deep yellow solution of $Pt(S_2CNR_2)_2PMePh_2$ formed slowly, from which the neutral 1:1 complex could be obtained, and prolonged exposure of the ionic complex to acetone (ε = 20.7) or diethyl ether (ε = 4.34) (24 hours) gave deep yellow solutions from which only the neutral 1:1 compound was obtained.

The ^1H n.m.r. spectra (Table 4.4) of these ionic compounds is of some interest. At room temperature (301 K) the solution of $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ in $CDCl_3$ was deep yellow, indicating the presence of $Pt(S_2CNEt_2)_2PMePh_2$ although integration of the

TABLE 4.4

^{1}H n.m.r. data (in $CDCl_3$) for the dithiocarbamate, xanthate and dithiophosphate complexes obtained with excess tertiary phosphine

	T/k	τ Value[a]					J(P-H)[d]	J(Pt-H)[e]
		Dithio-ligand			$CH_3(PR'_3)$[b]	Others[c]		
		CH_3[f]		CH_2[g]				
$Pt(S_2CNEt_2)_2$	301	8.70(3)[h]		6.40(2)				
$[Ph_3(PhCH_2)P]S_2CNEt_2$	301	8.86(3)		5.86(2)		Ph, 2.0-3.0(10)		
$[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$	301	8.80(6)	6.26[4][i]	6.09	8.16(3) (s) (br)			
						Ph, 2.4-2.6(10)		
	213	8.80(6)		6.37(2); 5.77(2)	8.09(3)		9.0[j]	34.0
$[Pt(S_2CNEt_2)(PMePh_2)_2]Cl, H_2O$	301	8.73(3)		6.36(2)	8.06(3)	Ph, 2.6(10); H_2O, 7.20(1)[k]	10.0	34.0
	253	8.73(3)		6.36(2)	8.06(3)	Ph, 2.6(10); H_2O, 7.00(1)[k]	10.0	34.0
$[Pt(S_2CNEt_2)(PMePh_2)_2]PF_6$	301	8.72(3)		6.38(2)	8.06(3)	Ph, 2.5(10)	10.0	35.0
$[Pt(S_2CNEt_2)(PMePh_2)_2]BPh_4$	301	8.84(3)		6.56(2)	8.30(3)	Ph, 2.5-3.2(20)	10.0	35.0
$[Pt(S_2CNEt_2)(PPh_3)_2]Cl, H_2O$	301	8.78(3)		6.40(2)		Ph, 2.6(15); H_2O, 7.80(1)[k]		
$[Pt(S_2CNEt_2)(PPh_3)_2]PF_6$	301	8.75(3)		6.42(2)		Ph, 2.6(15)		
$[Pt(S_2CNEt_2)(PPh_3)_2]BPh_4$	301	8.94(3)		6.68(2)		Ph, 2.5-3.2(25)		
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]Cl, H_2O$	301	8.62(3)		6.22(2)	8.20(6)	Ph, 2.6(5); H_2O, 8.10(1)[k]	10.0	35.0
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]BPh_4$	301	8.74(3)		6.40(2)	8.60(6)	Ph, 2.5-3.2(15)	10.0	34.0
$[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$	301	6.71(s)[6]	6.53(s)		8.30(3)(s)	Ph, 2.6(10)		
	213		6.65(3)(s); 6.39(3)(s)		8.10(3)	Ph, 2.6(10)	9.5[j]	35.0
$[Pt(S_2CNMe_2)(PMePh_2)_2]Cl, H_2O$	301		6.73(3) (s)		8.10(3)	Ph, 2.6(10); H_2O, 7.50(1)[k]	10.0[j]	35.0
	243		6.73(3) (s)		8.10(3)	Ph, 2.6(10); H_2O, 7.10(1)[k]	"	"
$[Pt(S_2CNMe_2)(PMePh_2)_2]BPh_4$	301		7.25(3) (s)		8.35(3)	Ph, 2.6-3.2(20)	10.0[j]	35.0
$[Pt(S_2CNMe_2)(PPh_3)_2]Cl, H_2O$	301		6.70(3) (s)			Ph, 2.5-2.7(15); H_2O, 7.9(1)[k]		
$[Pt(S_2CNMe_2)(PPh_3)_2]BPh_4$	301		7.40(3) (s)			Ph, 2.6-3.2(25)		

Table 4.4 page 2

		τ Value[a]					
		Dithio-ligand		$CH_3(PR'_3)$[b]	Others[c]	J(P-H)[d]	J(Pt-H)[e]
		CH_3[f]	CH_2[g]				
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]Cl, 2H_2O$	301	6.55(3) (s)		8.10(6)	Ph, 2.5(5); H_2O, 7.70(2)[k]	10.0[j]	35.0
$[Pd(S_2CNMe_2)(PMe_2Ph)_2]Cl, 2H_2O$	301	6.60(3) (s)		8.35(6) (s)	Ph, 2.6(5); H_2O, 7.80(2)[k]		
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]BPh_4$	301	7.05(3) (s)		8.65(6)	Ph, 2.6-3.2(15)	10.0[j]	37.0
$CH_2(S_2CNEt_2)_2$	313	8.83(6)	6.12(4) (s)		CH_2, 4.60(1) (s)		
	301	8.83(6)	6.28(2) 5.96(2)		CH_2, 4.60(1) (s)		
$CH_2(S_2CNMe_2)_2$	313	6.57(6) (s)	-		CH_2, 4.64(1) (s)		
	301	6.66(3) (s); 6.45(3) (s)	-		CH_2, 4.64(1) (s)		
$[Pt\{S_2P(OEt)_2\}(PPh_3)_2]BPh_4$	301	8.66(3)	5.88(2)[l]		Ph, 2.5-3.2(25)		
$(PPh_3)_2PtS_2P(O)OEt$	301	8.80(3)	6.05(2)[l]		Ph, 2.5-2.8(30)		
$[Pt(S_2COEt)(PPh_3)_2]BPh_4$	301	8.66(3)	5.58(2)		Ph, 2.5-3.2(50)		

s(singlet); d(doublet); br(broad)

[a] ±0.01. [b] Triplet of doublets unless otherwise stated. [c] Phenyl resonance; complex multiplet. [d] ±0.2Hz. [e] ±0.5Hz

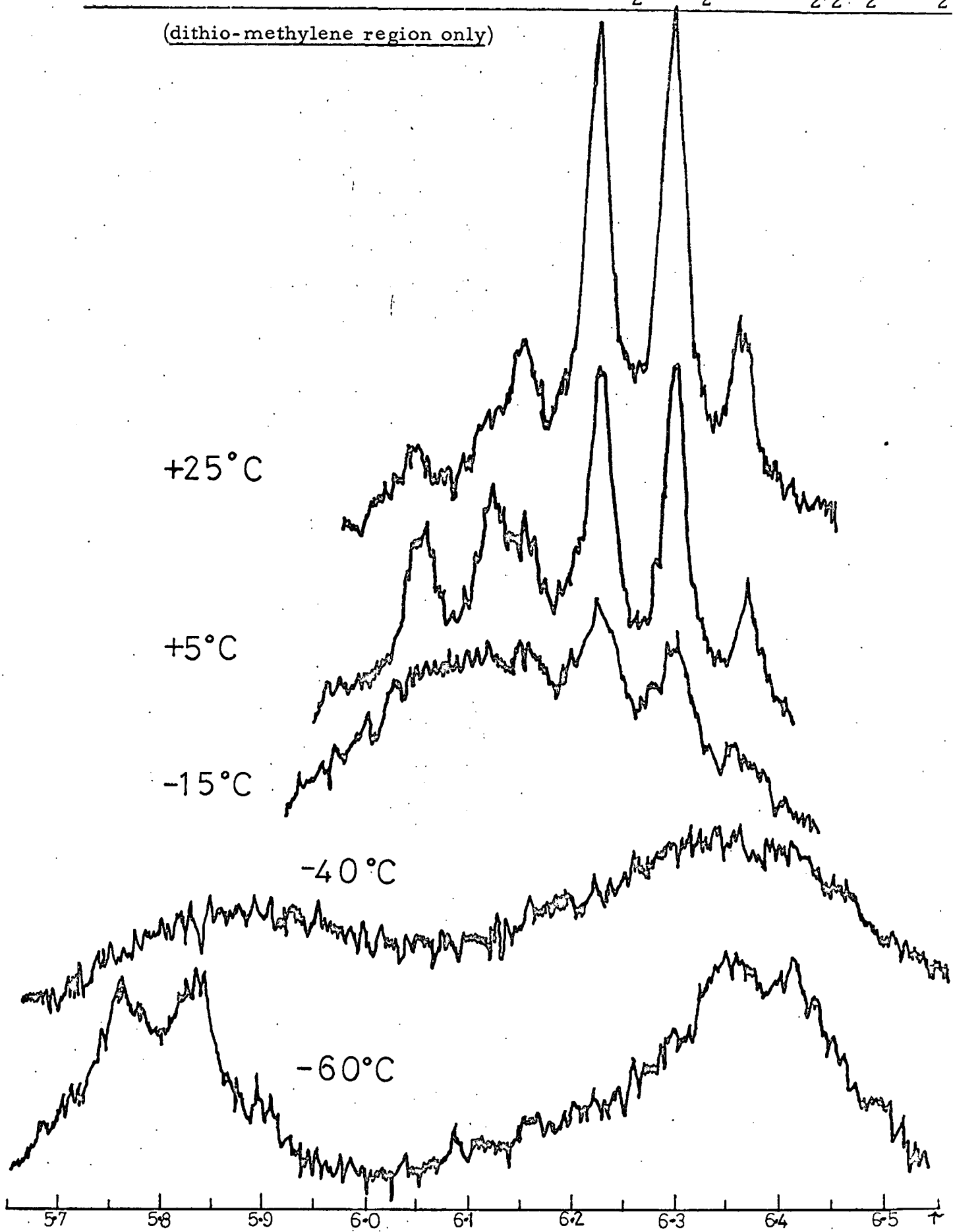
[f] Triplet unless otherwise stated ($J_{CH_2CH_3}$ 7.0Hz). [g] Quartet unless otherwise stated ($J_{CH_2CH_3}$ 7.0Hz). [h] Numbers in parenthesis indicate normalised integrated intensities. [i] Two resonances of total intensity [ ]. [j] Since $H_nPP'H'_n$ type spectrum, coupling constant is $J_{PH} + J_{PH'}$.

[k] τ Value is concentration dependent. [l] Overlapping doublet of quartets with $J_{CH_2CH_3}$ 7.0Hz; J_{CH_2-P} 9.4Hz

$^{-}S_2CNEt_2$ to $PMePh_2$ protons was that calculated for the ionic 1:2 complex. This suggested that appreciable dissociation of the ionic complex into the 1:1 complex and free phosphine occurred, and confirmation for this was shown by the ^1H n.m.r. spectrum (Figure 4.5). The CH_2-protons of the dithiocarbamate ligand showed an intense quartet at τ6.26 in an identical position to that found for $Pt(S_2CNEt_2)_2PMePh_2$ at room temperature, together with a smaller quartet centred at τ6.09 which was attributed to the ionic complex. In the phosphine region the broad singlet at τ8.16 indicated rapid exchange between free and coordinated phosphine (cf. the triplet of doublets centred at τ7.72 for $Pt(S_2CNEt_2)_2PMePh_2$. On cooling, however, the solution became progressively paler, indicating increasing concentration of the ionic complex, and the ^1H n.m.r. spectrum showed a growth in the quartet at τ6.09 (attributed to the ionic complex), together with a decrease in intensity of the quartet at τ6.29 (due to 1:1 complex). At 273 K, the two quartets were of comparable intensity, but at 263 K the low field quartet at τ6.09 began to broaden while that at high field remained sharp. By 253 K, a single broad resonance was observed, and further lowering of the temperature to 213 K produced two quartets at τ6.37 and 5.77 (separation 60 Hz). The resonance at τ6.37 was close to that previously found for the bidentate ligand, while that at low field (τ5.77) was attributed to the ionic ligand. The process was found to be completely reversible and raising the temperature to 301 K produced the initial deep yellow solution (Figure 4.5).

FIGURE 4.5

Variable Temperature ^{1}H n.m.r. spectra of $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$

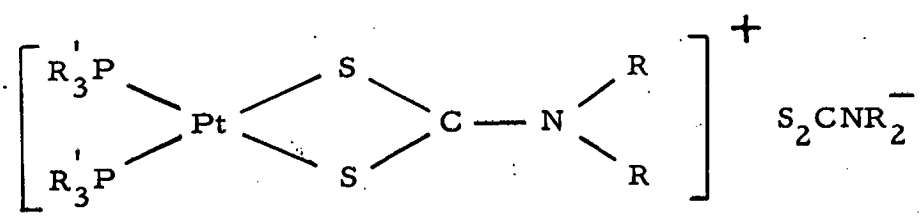


The ^{1}H n.m.r. spectra were interpreted in terms of an equilibrium between the ionic species and the 1:1 complex (plus free phosphine) as indicated in equation (2)

$$[Pt(S_2CNR_2)(PR'_3)_2]S_2CNR_2 \rightleftharpoons Pt(S_2CNR_2)_2PR'_3 + PR'_3 \qquad (2)$$

which lay well to the right hand side at room temperature. The ^{1}H n.m.r. changes down to ca 253 K could then be explained by a shift towards the left hand side of this equilibrium. By estimating the relative concentrations of the two species at various temperatures from room temperature to 256 K, the equilibrium constant could be calculated approximately and gave K_{300K} 0.33 mol l^{-1}, ΔH 60kJ mol^{-1}, ΔS 191 J $K^{-1}mol^{-1}$. A similar temperature-dependent equilibrium between the 1:1 and ionic species was observed in the solution i.r. studies of $[Pd(S_2PPh_2)(PEt_3)_2]S_2PPh_2$ at varying temperatures (cf. Chapter 2 and reference 52).

Below 265 K, the ^{1}H n.m.r. changes were interpreted as a slowing down of the exchange between ionic and bidentate dithiocarbamate groups, such that at 213 K the spectrum corresponded to that expected for a frozen-out ionic structure (6),



(6)

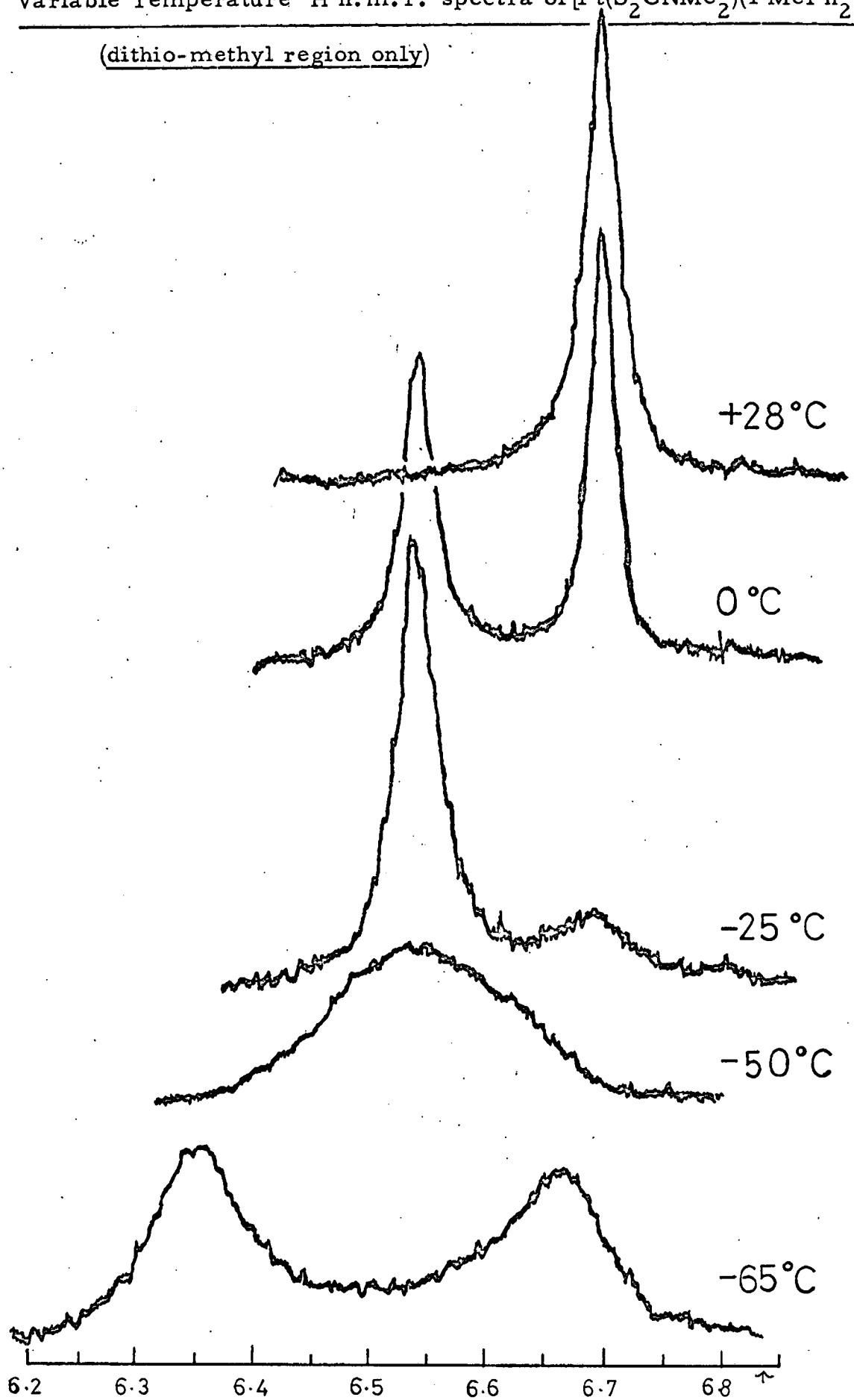
and the absence of the quartet at τ6.17 at 213 K showed that the equilibrium lay completely to the left hand side at this temperature. Further evidence for the presence of only the ionic species at this temperature was shown by the tertiary phosphine resonance where a strong doublet at τ8.09 with weak ^{195}Pt satellites was found, in contrast to the exchange observed at room temperature. The low temperature phosphine resonance also supported the cis phosphine arrangement. An estimate for the activation energy for the interchange of ionic and bidentate groups, obtained from the coalescence temperature gave ΔG^*_{253K} 51.2 kJ mol^{-1} (Table 4.2)[61].

Variable temperature ^1H n.m.r. spectra of $[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$ in $CDCl_3$ showed closely similar behaviour, namely, a single dithiocarbamate methyl resonance (τ6.71) at 301 K corresponding to $Pt(S_2CNMe_2)_2PMePh_2$, and when the temperature was lowered growth of the peak at τ6.53 (ionic complex) followed by broadening (ca 220 K) and splitting into two equivalent resonances at τ6.65 and 6.39 (separation 26 Hz) (ca 213 K) which were assigned to the bidentate and ionic dithiocarbamate methyl resonances respectively (see Figure 4.6). Analysis of the higher temperature region gave K_{300K} 0.22 mol l^{-1}, ΔH 69 kJ mol^{-1}, ΔS 218 J K^{-1} mol^{-1} for the equilibrium between 1:1 and ionic species, and an estimation for the ionic-bidentate ligand exchange was obtained from the coalescence temperature and gave ΔG^*_{223K} 46.5 kJ mol^{-1} (Table 4.2)[61].

FIGURE 4.6

Variable Temperature ^{1}H n.m.r. spectra of $[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$

(dithio-methyl region only)



b) Preparation of the complexes $[M(S_2CNR_2)(PR'_3)_2]Cl, H_2O$

When a suspension of $Pt(S_2CNR_2)_2$ in dichloromethane was treated with an excess of tertiary phosphine, an initial yellow solution was produced which slowly decolourised after several hours, the qualitative rate of decolourisation being $PMe_2Ph \simeq PMePh_2 > PPh_3$. During this stage, a steady rise in conductivity was observed, giving a final value corresponding to that expected for a 1:1 electrolyte (Tables 4.3 and 4.5). Concentration of the solvent and addition of diethyl ether gave white crystalline solids. Treatment of $Pd(S_2CNMe_2)_2$ with an excess of PMe_2Ph gave the corresponding pale yellow palladium product, but attempted synthesis of other tertiary phosphine complexes of palladium has proved unsuccessful.

The $PMePh_2$ complexes (of platinum) could also be obtained by shaking $[Pt(S_2CNR_2)(PMePh_2)_2]S_2CNR_2$ in dichloromethane or chloroform (solvent grade with ethanol stabiliser). The initial deep yellow solution, containing a mixture of ionic and 1:1 complexes together with free $PMePh_2$, slowly decolourised, giving an increase in the conductivity. Removal of the solvent from the final colourless solution, and addition of diethyl ether gave the white product. However, no decolourisation in $CDCl_3$ or ethanol-free $CHCl_3$ occurred.

Conductivity measurements in dichloromethane showed the complexes were 1:1 electrolytes. The ^1H n.m.r. spectra showed single dithiocarbamate resonances, close to the value previously found for the bidentate ligand, which remained unchanged on cooling. Integration of the dithiocarbamate to phosphine protons, together with

the chemical shifts and coupling constants found for the $PMePh_2$ and PMe_2Ph compounds strongly supported the formulation $[Pt(S_2CNR_2)(PR'_3)_2]X$ for the compounds where X was an anion not containing protons (except for the presence of an additional weak resonance found in the ^1H n.m.r. spectra, in the region 6-8τ, which will be considered later).

Exchange of the anion X in the complexes was easily obtained by reaction with $NaBPh_4$ or NH_4PF_6 in acetone-methanol solution, and the products obtained $[Pt(S_2CNR_2)(PR'_3)_2]Y$ ($Y=BPh_4, PF_6$) showed the expected behaviour as 1:1 electrolytes in dichloromethane (Table 4.3) and no loss of the dithiocarbamate resonance in the ^1H n.m.r. spectra. (The upheld shift of both the dithiocarbamate and phosphine resonances (ca 0.2 p.p.m.) in the BPh_4^- compounds compared with the PF_6^- and X^- complexes were attributed to a ring-current effect in the BPh_4^- complexes, similar to that found for $[Pt(S_2PMe_2)(PR'_3)_2]Y$ complexes [61].)

Attempted exchange of the anion X by chloride ion, by shaking the complexes in dichloromethane with chloride anion-exchange resin yielded products which were shown by i.r. spectra, ^1H n.m.r. spectra and melting points to be identical with the original complex, which indicated the possibility of chloride in the anion X. This was confirmed by direct analysis and ESCA measurements.

Examination of the ^1H n.m.r. spectra of the complexes $[Pt(S_2CNR_2)(PR'_3)_2]X$ showed that the position of the additional weak resonance in the region τ6-8 varied with solvent, solute concentration

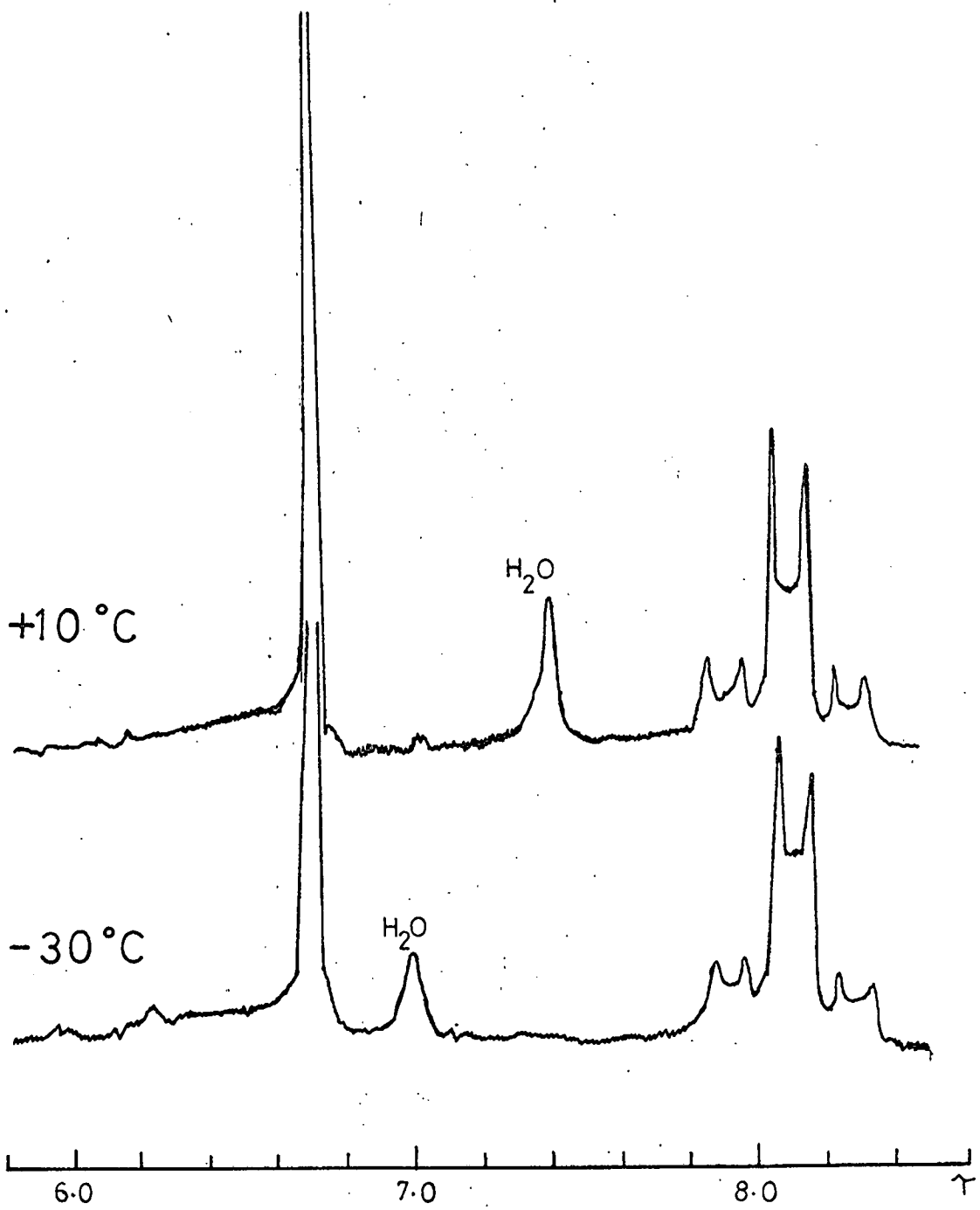
and temperature; on lowering the temperature (Figure 4.7), or increasing the concentration or solvent polarity, the peak shifted to lower field. This behaviour strongly indicated the presence of a hydrogen-bonded species. Investigation of the mull i.r. spectra of the complexes revealed very weak O-H stretching vibrations (ca 3400 cm^{-1}) and bending vibrations (ca 1620 cm^{-1}), and together with the similarity of the position of the weak resonance in the ^1H n.m.r. with that recently reported for $[Co(CO)_2(PPh_3)_2(H_2O)Cl]$ [84] (T7.4), supported the presence of a water molecule. This was confirmed by direct analysis and ESCA measurements, and the complexes $[Pt(S_2CNR_2)(PR'_3)_2]X$ were reformulated as $[Pt(S_2CNR_2)(PR'_3)_2]Cl, H_2O$ (with the exception of $[M(S_2CNMe_2)(PMePh_2)_2]Cl, \frac{1}{2}H_2O$, M = Pd, Pt). Since the addition of excess chloride ion produced no change in the hydrogen-bonded resonance in the ^1H n.m.r. spectra, it appeared unlikely that the water molecule was hydrogen-bonded to the cation.

Clearly the only source of chloride ion was the dichloromethane solvent, and from the ethereal washings obtained in the preparation of $(Pt(S_2CNR_2)(PR'_3)_2]Cl, H_2O$, a benzene soluble organo-thio compound was isolated which was identified by elemental analysis, ^1H n.m.r., and mass spectra as $CH_2(S_2CNR_2)_2$ (R=Me, Et).

An attempted preparation of the ethyl compound by refluxing sodium diethyldithiocarbamate with anhydrous dichloromethane (recently reported to give high yields [85]) produced a very low yield unless the reagents were scrupulously dried. However, the compound was readily prepared in high yield by shaking a mixture of $NaS_2CNEt_2, 3H_2O$ (as

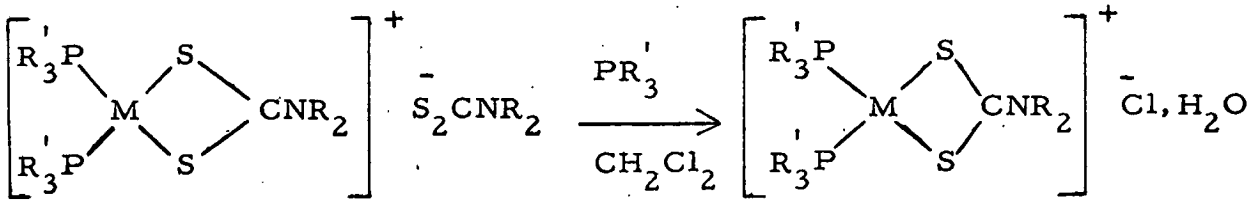
FIGURE 4.7

Variable Temperature ^{1}H n.m.r. spectra of $[Pt(S_2CNMe_2)(PMePh_2)_2]Cl.H_2O$



obtained) with dichloromethane (solvent grade) together with any tertiary phosphine (PPh_3, $PMePh_2$ or PMe_2Ph) for 24 hours, followed by solvent removal, and trituration of the resultant oil with light petroleum (b.p. 60-80°). The tertiary phosphine thus facilitated the formation of $CH_2(S_2CNEt_2)_2$. The ^1H n.m.r. spectra showed two non-equivalent ethyl groups at room temperature which coalesced at higher temperature (Table 4.4). The estimated free energy of activation for the barrier to free rotation about the C-N bond (obtained from the coalescence temperature [61]) (Table 4.2) was found to be close to that previously reported for EtS_2CNEt_2 [79]. The methyl compound $CH_2(S_2CNMe_2)_2$ was prepared by the same method, and showed similar behaviour in the ^1H n.m.r. spectra (Table 4.4). In the absence of phosphine, the only product obtained was tetramethylthiuram disulphide $(Me_2NCS_2)_2$.

It appeared likely that the chloride complex was obtained (in CH_2Cl_2 solvent) <u>via</u> prior formation of the ionic dithiocarbamate complex, followed by reaction with the solvent (catalysed by the presence of free tertiary phosphine) as shown in equation (3).



$$+ CH_2(S_2CNR_2)_2 \qquad (3)$$

This mechanism was supported by the preparation of the chloride complex by reaction of the ionic dithiocarbamate complex $[Pt(S_2CNR_2)(PR'_3)_2]S_2CNR_2$ with CH_2Cl_2 (where the free phosphine is present as a result of dissociation to the 1:1 complex) and also by the isolation of $CH_2(S_2CNR_2)_2$ from the reaction of the dithiocarbamate ion in CH_2Cl_2 in the presence of tertiary phosphines.

No investigation of the side products obtained using chloroform (with ethanol-stabiliser) as solvent was made, but it seems likely that traces of the ethoxy ion may have facilitated the formation of the halide ion from the solvent.

4.5 Reaction of Platinum xanthates and dithiophosphates with an excess of tertiary phosphines.

Reaction of $Pt(S_2COEt)_2$ with excess PPh_3 in CH_2Cl_2 produced immediate decolourisation of the solution. This was accompanied by a rapid increase in the conductivity, to a maximum value corresponding to ca two-thirds of that expected for a 1:1 electrolyte, followed (within minutes) by a steady decrease in the conductivity (Table 4.5). Removal of the solvent and addition of light petroleum (b.p. 60-80°C) gave the produce $(PPh_3)_2PtS_2CO$ previously obtained by Fackler et al.[40] When the reaction was attempted in nitromethane, conductivity measurements showed a maximum value close to that expected for a 1:1 electrolyte, but the conductivity steadily decreased with time (Table 4.5). The conductivity strongly indicated the formation of an ionic species as an intermediate but all attempts to isolate this by immediate addition of light petroleum (added 20 sec. after mixing) gave

TABLE 4.5

Variation of Equivalent conductivity with time for some platinum(II) dithio-compounds

$[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$ (7.1×10^{-4}M) in CH_2Cl_2

Time (min)	0	1.0	3.0	5.0	15.0	30.0	∞ [a]
Λ [b]	10.4 [c]	13.5	22.3	27.1	36.9	41.8	50.1 [d]

$[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ (10.7×10^{-4}M) in CH_2Cl_2

Time(min)	0	15.0	∞ [a]
Λ [b]	16.4 [c]	42.2 [d]	45.0

$Pt(S_2COEt)_2$ (10×10^{-4}M) + excess PPh_3 in CH_2Cl_2

Time(min)	0	0.25	0.5	1.0	3.0	15.0
Λ [b]	15.7	13.7	13.2	12.5	9.2	7.0

$Pt(S_2COEt)_2$ (30×10^{-4}M) + excess PPh_3 in CH_3NO_2

Time(min)	0	3.0	6.0	10.0	26.0	35.0	60
Λ [b]	90	80	71	61	50	33	19

[a] 24 hours. [b] In $\Omega^{-1}cm^2mol^{-1}$. [c] Yellow solution of $[Pt(S_2CNR_2)(PMePh_2)_2]S_2CNR_2$, $Pt(S_2CNR_2)_2PMePh_2$, and $PMePh_2$. [d] Decolourised solution containing $[Pt(S_2CNR_2)(PMePh_2)_2]Cl$, H_2O and $CH_2(S_2CNR_2)_2$.

the 1:1 product $Pt(S_2COEt)_2PPh_3$ and a little $(PPh_3)_2PtS_2CO$.

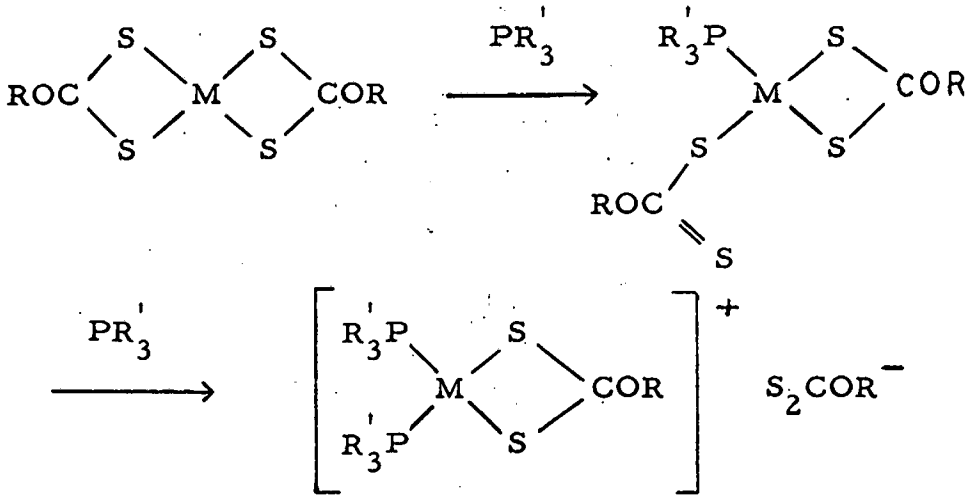
However, when an aqueous solution of $NaBPh_4$ was added immediately (30 sec.) after mixing $Pt(S_2COEt)_2$ (in acetone-methanol solution) with excess PPh_3 (dissolved in a minimum volume of acetone) a white precipitate of $[Pt(S_2COEt)(PPh_3)_2]BPh_4$ was formed, which was characterised by ^1H n.m.r. (Table 4.4), analysis and conductivity (Table 4.3). The isolation of this product strongly supported the existence of an ionic species in the reaction mixture.

Similarly, the reaction of $Pt[S_2P(OEt)_2]_2$ with an excess of PPh_3 in CH_2Cl_2 produced rapid decolourisation of the solution. In this instance, the conductivity of the final solution corresponded to that of a 1:1 electrolyte, and no decrease in the conductivity with time was observed. However, all attempts to isolate the ionic species by rapid removal of the solvent gave only the product $(PPh_3)_2PtS_2P(O)OEt$, also previously reported by Fackler et al.[40]. Addition of diethyl ether to the conducting solution also isolated this product together with some $Pt[S_2P(OEt)_2]_2PPh_3$. As with the xanthate reaction, it was possible to obtain the complex $[Pt\{S_2P(OEt)_2\}(PPh_3)_2]BPh_4$ by rapid addition of $NaBPh_4$ to an acetone-methanol mixture of the tertiary phosphine (in excess) and $Pt[S_2P(OEt)_2]_2$.

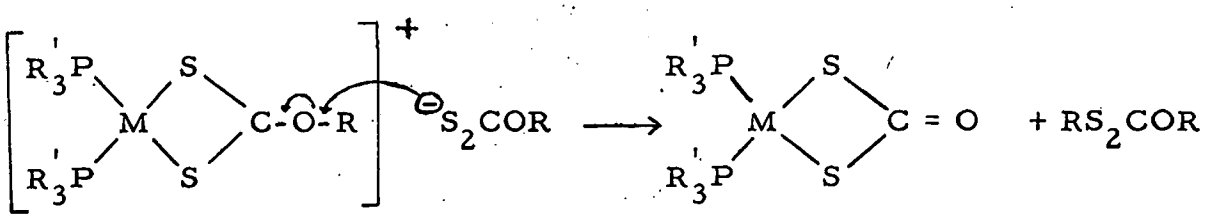
The conductivity measurements, together with the isolation of the BPh_4 complexes strongly indicated the existence of an ionic species from the reaction of platinum xanthate or dithiophosphate with excess phosphine, although the unexpected products $(PPh_3)_2PtS_2CO$ or $(PPh_3)_2PtS_2P(O)OEt$ (together with organic side products) were

obtained from the reaction. These products could, however, be rationalised by considering the following mechanisms:-

For the xanthate reaction,

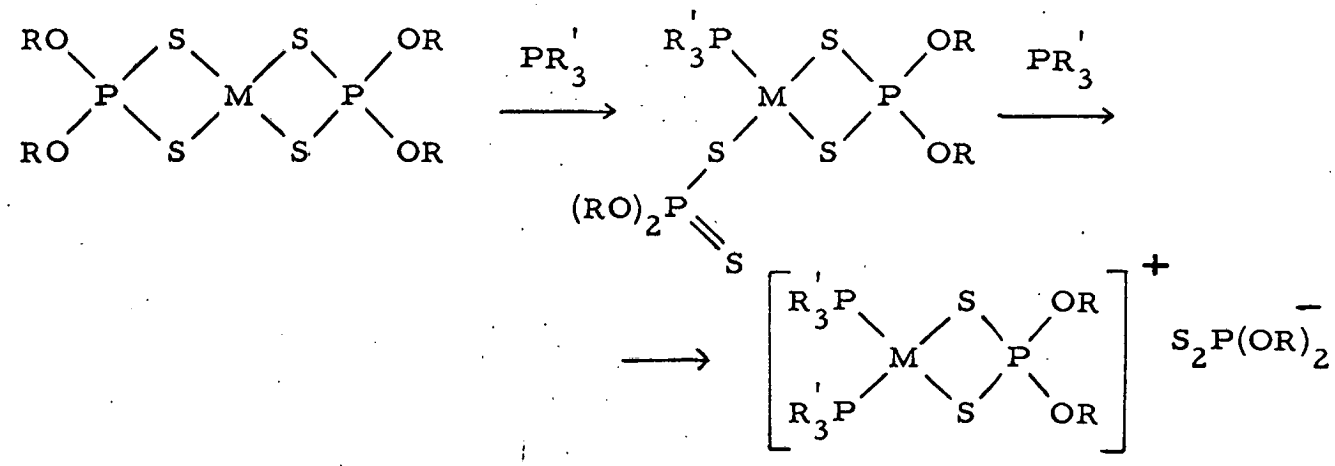


and then,

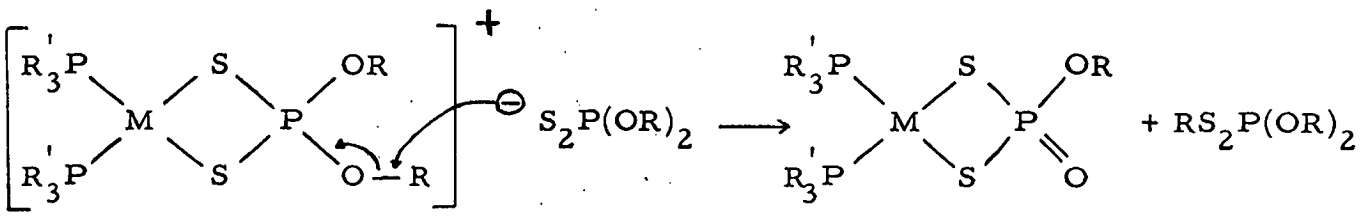


i.e. stepwise cleavage of the metal-sulphur bonds of one of the chelate rings to produce the ionic xanthato complex, is followed by nucleophilic attack by the xanthate anion on the alkoxy-group of the coordinated xanthate group, giving the neutral dithiocarbonate complex and a xanthate ester (both of which were previously isolated by Fackler et al. from the reaction [40]).

Similarly for the dithiophosphate reaction



and then,



the ionic complex is produced as an intermediate which after nucleophilic attack by the dithiophosphate anion on the alkoxy group of the coordinated dithiophosphate would yield the observed products.

Besides accounting for the final products, conducitvity values and isolation of BPh_4^- complexes, this mechanism also rationalises several of Fackler's earlier observations. For instance, the observed inhibition of the reaction in carbon disulphide (relative to chloroform) is readily explained by the requirement of a fairly polar solvent to promote both the formation and stabilisation of an ionic intermediate. The observation that platinum xanthates or dithiophosphates undergo this reaction more readily than their palladium analogues, is consistent with the greater tendency of platinum to form the ionic complexes $[Pt(S\text{-}S)(PR'_3)_2]^+ (S\text{-}S)^-$ (cf. $^-S_2PPh_2$ studies in Chapter 2).

In the xanthate reactions the fact that the ethyl group is eliminated less readily than the benzyl group can be explained by the greater stability of the benzylcarbonium ion generated in the transition state.

4.6 Experimental

Analyses, molecular weights, i.r., ^{1}H n.m.r., mass spectra, conductivities and melting points were obtained as described in Chapter 2. Analytical data for many of the new compounds are given in Table 4.6. I am grateful to Dr. M. Barber and Mr. P. Swift of A.E.I. Scientific Apparatus Ltd. for the ESCA measurements. Materials:- Potassium tetrachloroplatinate (II) and palladium (II) chloride (Johnson Matthey); triphenylphosphine, dimethylphenylphosphine, sodium diethyldithiocarbamate (B.D.H.); dimethyldithiocarbamate (Ralph Emanuel). The other tertiary phosphines were prepared by standard literature methods.

Dithiocarbamate complexes

Bis(NN-dimethyldithiocarbamato)platinum (II). Potassium tetrachloroplatinate (II) in a minimum volume of hot water was mixed with an ethanolic solution of an excess of sodium NN-dimethyldithiocarbamate and shaken for 24 hours. The yellow product was filtered off, washed with water and ethanol, and air-dried; m.p. 305-308°C (Found: C, 16.8; H, 2.9; N, 6.3. Calculated for $C_6H_{12}N_2PtS_4$: C, 16.6; H, 2.8; N, 6.4 %).

Bis(NN- diethyldithiocarbamato)platinum (II)[33] was prepared in the

same way using K_2PtCl_4 and $NaS_2CNEt_2, 3H_2O$ (m.p. 245-250°C).[33] [62]

Bis(NN-dimethyldithiocarbamato)palladium (II). Palladium acetate was dissolved in benzene-dichloromethane and shaken for several hours with an ethanolic solution containing an excess of $NaS_2CNMe_2, 2H_2O$. The yellow precipitate was filtered off, washed with water and ethanol, and air-dried (Found: C, 20.3; H, 3.3; N, 7.5. Calculated for $C_6H_{12}N_2PdS_4$: C, 20.8; H, 3.5; N, 8.1 %).

Bis(NN- diethyldithiocarbamato)triphenylphosphine platinum (II). Bis(NN- diethyldithiocarbamato)platinum (II) was suspended in carbon disulphide and treated with triphenyl phosphine (<1:1 molar ratios). An orange-yellow solution was formed immediately, together with some unchanged $Pt(S_2CNEt_2)_2$ (which was removed by filtration). Partial removal of the solvent, followed by cooling (200 K) gave the yellow crystalline product; this was washed with diethyl ether, and dried in vacuo.

Bis(NN-diethyldithiocarbamato)methyl(diphenylphosphine)platinum (II) was prepared in the same way, using a deficiency of $PMePh_2$ under nitrogen, giving bright yellow crystals.

The products were soluble in chloroform, dichloromethane, carbon disulphide, and benzene; and insoluble in ethanol, acetone and dimethylsulphoxide. Attempted preparation of $Pt(S_2CNMe_2)_2PMePh_2$ by the previous method gave a mixture of this product and the ionic species $[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$. Preparation of the PMe_2Ph complexes was complicated by the side-reaction between the phosphine and CS_2[76]. Attempted preparation of $Pt(S_2CNMe_2)_2PPh_3$

or $Pt(S_2CNMe_2)_2AsPh_3$ by the previous method using an excess of the ligand gave yellow solutions very slowly (12 hrs) but the 1:1 products could not be isolated.

(NN-Diethyldithiocarbamato)bis(methyldiphenylphosphine)platinum (II) NN-Diethyldithiocarbamate. $Pt(S_2CNEt_2)_2$ (0.90 mmol) in acetone (5 ml) was treated with an excess of methyldiphenylphosphine (1.0 ml, 4.0 mmol) to give an immediate yellow solution from which yellow crystals of the product rapidly separated. These were washed with light petroleum (b.p.40-60°) and dried in vacuo (40°C).

(NN-Dimethyldithiocarbamato)bis(methyldiphenylphosphine)platinum (II) NN-Dimethyldithiocarbamate was made by the same method. These compounds are very unstable and readily rearrange to form $Pt(S_2CNR_2)_2PMePh_2$ and $PMePh_2$ on prolonged exposure to benzene, diethyl ether or acetone. Attempts to make the corresponding triphenylphosphine and dimethylphenylphosphine ionic species were unsuccessful. The former gave only $Pt(S_2CNEt_2)_2PPh_3$ and the latter an intractable oil.

(NN-Diethyldithiocarbamato)bis(methyldiphenylphosphine)platinum (II) chloride monohydrate.

Method (A). $Pt(S_2CNEt_2)_2$ in dichloromethane (dried over $MgSO_4$) was treated with a three-fold excess of $PMePh_2$ under nitrogen. The initial yellow solution slowly became colourless (ca 1-2 h), and concentration in vacuo followed by addition of an excess of diethyl ether gave a white microcrystalline precipitate of the product. This was washed with diethyl ether and dried in vacuo (40°C).

Method (B). The same compound was also made by prolonged exposure of $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ to dichloromethane. The initial deep yellow solution slowly became colourless (ca 2 h) and concentration of the solution, followed by addition of an excess of diethyl ether gave the product.

(NN-Diethyldithiocarbamato)bis(dimethylphenylphosphine)platinum (II) chloride monohydrate. Method as in procedure (A) above, from $Pt(S_2CNEt_2)_2$ and excess PMe_2Ph, gave a white product.

(NN-Diethyldithiocarbamato)bis(triphenylphosphine)platinum (II) chloride monohydrate. Method as above, from $Pt(S_2CNEt_2)_2$ and excess PPh_3, gave a white product.

(NN-Dimethyldithiocarbamato)bis(methyldiphenylphosphine)platinum (II) chloride monohydrate.

Method (A). $Pt(S_2CNMe_2)_2$ in dichloromethane (dried over $MgSO_4$) was treated with a three-fold excess of $PMePh_2$ under nitrogen. The initial yellow solution slowly became colourless (ca 1-2h) and concentration in vacuo, followed by precipitation with either diethyl ether or light petroleum (b.p. 60-80°C) gave a mixture of $[Pt(S_2CNMe_2)(PMePh_2)_2]Cl, H_2O$ and $CH_2(S_2CNMe_2)_2$. The latter was removed by careful washing with benzene, and the remaining crystalline product was washed with diethyl ether and dried in vacuo (40°).

Method (B). Prolonged exposure of $[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$ in CH_2Cl_2 caused the initial deep yellow solution to become colourless (ca 2h). Precipitation with diethyl ether, and extraction of $CH_2(S_2CNMe_2)_2$ with benzene gave the white product.

(NN-Dimethyldithiocarbamato)bis(phenyldimethylphosphine)platinum (II) chloride monohydrate. Method as in procedure (A) above, from $Pt(S_2CNMe_2)_2$ and an excess of PMe_2Ph, gave a white product.

(NN-Dimethyldithiocarbamato)bis(triphenylphosphine)platinum (II) chloride monohydrate. Method as above, from $Pt(S_2CNMe_2)_2$ and an excess of PPh_3, gave a white product.

(NN-Dimethyldithiocarbamato)bis(ethyldiphenylphosphine)platinum (II) chloride monohydrate. Method as above, from $Pt(S_2CNMe_2)_2$ and an excess of $PEtPh_2$, gave a white product.

(NN-Dimethyldithiocarbamato)bis(phenyldimethylphosphine)palladium (II) chloride dihydrate. Method as above. Excess of PMe_2Ph added to $Pd(S_2CNMe_2)_2$ gave an initial orange solution which slowly became yellow (ca 2h). Precipitation with ether and extraction of $CH_2(S_2CNMe_2)_2$ with benzene, gave a yellow product; m.p. 83-85°. (Found: C, 38.4; H, 5.0; N, 2.9. Calculated for $C_{19}H_{32}NP_2ClO_2PdS_2$: C, 39.8; H, 5.6; N, 2.4 %).

Attempted preparation of $[Pd(S_2CNMe_2)(PPh_2Me)_2]Cl, nH_2O$ by the same method gave a pale precipitate which became sticky on filtering.

(NN-Diethyldithiocarbamato)bis(methyldiphenylphosphine)platinum (II) tetraphenylborate. $[Pt(S_2CNEt_2)(PMePh_2)_2]Cl, H_2O$ dissolved in a minimum volume of ethanol was treated with a concentrated aqueous solution of $NaBPh_4$ giving an immediate white precipitate. This was filtered off, washed well with water and light petroleum (b.p. 60-80°C) and dried in vacuo (40°). The product was also obtained by reaction

between $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ and $NaBPh_4$ in methanol.

(NN-Diethyldithiocarbamato)bis(phenyldimethylphosphine)platinum (II) tetraphenylborate. Method as above, from $[Pt(S_2CNEt_2)(PMe_2Ph)_2]Cl, H_2O$ (in minimum acetone) and an excess of $NaBPh_4$ (aqueous solution) gave a white product.

(NN-Diethyldithiocarbamato)bis(triphenylphosphine)platinum (II) tetraphenylborate. Method as above, from $[Pt(S_2CNEt_2)(PPh_3)_2]Cl, H_2O$ (in ethanol) and $NaBPh_4$ (concentrated aqueous solution), gave a white product.

(NN-Dimethyldithiocarbamato)bis(methyldiphenylphosphine)platinum (II) tetraphenylborate. Method as above, from $[Pt(S_2CNMe_2)(PMePh_2)_2]Cl, H_2O$ (in a minimum volume of acetone) and an excess of $NaBPh_4$ (concentrated aqueous solution), gave a white product. The product was also obtained by reaction between $[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$ and $NaBPh_4$ in methanol.

(NN-Dimethyldithiocarbamato)bis(phenyldimethylphosphine)platinum (II) tetraphenylborate. Method as above, from $[Pt(S_2CNMe_2)(PMe_2Ph)_2]Cl, H_2O$ (in a minimum volume of acetone) and an excess of $NaBPh_4$ (concentrated aqueous solution) gave a white product.

(NN-Dimethyldithiocarbamato)bis(ethyldiphenylphosphine)platinum (II) tetraphenylborate. Method as above, from $[Pt(S_2CNMe_2)(PEtPh_2)_2]Cl, H_2O$ and an excess of $NaBPh_4$, gave a white product.

(NN-Dimethyldithiocarbamato)bis(triphenylphosphine)platinum (II) tetraphenylborate. Method as above, from $[Pt(S_2CNMe_2)(PPh_3)_2]Cl, H_2O$ (in a minimum volume of methanol) and an excess of $NaBPh_4$ in a

minimum volume of acetone), gave a white product.

(NN-Dimethyldithiocarbamato)bis(phenyldimethylphosphine) palladium (II) tetraphenylborate. Method as above, from $[Pd(S_2CNMe_2)(PMe_2Ph)_2]Cl, 2H_2O$ (in a minimum volume of acetone) and an excess of $NaBPh_4$ (concentrated aqueous solution), gave a pale yellow product. (m.p. 126-130°C. Found: C, 64.7; H, 5.9; N, 1.8. Calculated for $C_{34}H_{48}NP_2S_2BPd$: C, 62.9; H, 5.9; N, 1.7 %).

(NN-Diethyldithiocarbamato)bis(methyldiphenylphosphine)platinum (II) hexafluorophosphate. $[Pt(S_2CNEt_2)(PMePh_2)_2]Cl, H_2O$ in acetone-methanol solution was added to an aqueous solution of ammonium hexafluorophosphate to give a white colloidal precipitate. Partial removal of the solvent in vacuo gave a white powder which was washed in water and light petroleum (b.p. 60-80°C), and dried in vacuo (40°C).

(NN-Diethyldithiocarbamato)bis(triphenylphosphine)platinum (II) hexafluorophosphate. $[Pt(S_2CNEt_2)(PPh_3)_2]Cl, H_2O$ in methanol was added to an aqueous solution of NH_4PF_6 and gave an immediate white precipitate of the product, which was washed in water and light petroleum (b.p. 60-80°C) and dried in vacuo.

(NN-Dimethyldithiocarbamato)bis(methyldiphenylphosphine)platinum (II) hexafluorophosphate. Method as for ethyl analogue, from $[Pt(S_2CNMe_2)(PMePh_2)_2]Cl, H_2O$ in ethanol with NH_4PF_6 (aqueous solution), gave a white product.

Methylene bis(NN-diethyldithiocarbamate)

A mixture of $NaS_2CNEt_2, 3H_2O$, dichloromethane (solvent grade as obtained) and a tertiary phosphine (PPh_3, $PMePh_2$ or PMe_2Ph) was

shaken for 24h. Solvent removal and trituration of the resulting oil with light petroleum (b.p. 60-80°C) gave the product, which was characterised by m.p. and mass and ^{1}H n.m.r. spectroscopy[85]. The same compound was also formed (but in lower yield) when the reaction was carried out in the absence of PR'_3.

The product could also be obtained from the ethereal filtrates obtained during preparation of the complexes $[Pt(S_2CNEt_2)(PR'_3)_2]Cl, H_2O$. Removal of the solvent from the filtrates gave an oil, which on trituration with light petroleum (b.p. 60-80°C) gave the white crystalline product (m.p. 70-71°C. Found: C, 42.6; H, 7.2; N, 9.0. Calculated for $C_{11}H_{22}N_2S_4$: C, 42.6; H, 7.1; N, 9.0 %).

Methylene bis(NN-dimethyldithiocarbamate)

A mixture of NaS_2CNMe_2, CH_2Cl_2 and tertiary phosphine (PPh_3, $PMePh_2$ or PMe_2Ph) was shaken for 24 hours, and the product obtained as in the preparation above. In the absence of tertiary phosphine, only tetramethylthiuramdisulphide (Found: C, 31.3; H, 5.2; N, 11.9. Calc. for $C_6H_{12}N_2S_4$: C, 30.0; H, 5.0; N, 11.7 %) and NaS_2CNMe_2 were detected.

The product could also be obtained from the benzene washings obtained during preparation of the complexes $[M(S_2CNMe_2)(PR'_3)_2]Cl, nH_2O$ (M=Pd, Pt; PR'_3=PPh_3, $PMePh_2$, PMe_2Ph, $PEtPh_2$; n=1 or 2 as described previously). Removal of the solvent and treatment with light petroleum gave the white crystalline product. (m.p. 93-96°C. Found: C, 33.7; H, 5.2; N, 10.9. Calculated for $C_7H_{14}N_2S_4$: C, 33.1; H, 5.1; N, 11.0 %)

Mass spectrum: 254 $[CH_2(S_2CNMe_2)_2^+]$, 166$[Me_2NCS_2CH_2S^+]$ and 88$[Me_2NCS^+]$ (cf. reference 85).

OO'-Diethyl Dithiophosphate Complexes

Bis(OO'-diethyldithiophosphate)platinum (II) was prepared as described earlier[33] from K_2PtCl_4 and $NH_4S_2P(OEt)_2$[86]. (m.p.124°C. Found: C,17.2; H,3.5. Calculated for $C_8H_{20}O_4P_2PtS_4$: C,17.0;H,3.6 %).

Bis(OO'-diethyldithiophosphato)triphenylphosphine platinum (II)

$Pt[S_2P(OEt)_2]_2$ was shaken with triphenylphosphine (1:1 molar ratios) in dichloromethane to give a lemon-yellow solution. Slow evaporation of the solvent in the presence of an excess of light petroleum (b.p. 40-60°C) gave yellow crystals of the product.

$Pt[S_2P(OEt)_2]_2AsPh_3$ was prepared *in situ* by reaction of $Pt[S_2P(OEt)_2]_2$ and an excess of $AsPh_3$ in $CDCl_3$.

O-Ethyldithiophosphato bis(triphenylphosphine)platinum (II)

$Pt[S_2P(OEt)_2]_2$ and PPh_3 (*ca* 1:3 molar ratios) were refluxed in $CHCl_3$ for *ca* 3 hours, during which time the initial yellow solution slowly became colourless. Removal of the solvent and addition of diethyl ether gave a white product.

Reaction of $Pt[S_2P(OEt)_2]_2$ and an excess of PPh_3 in CH_2Cl_2 rapidly gave a colourless conducting solution, presumably containing the ionic complex $[Pt\{S_2P(OEt)_2\}(PPh_3)_2]S_2P(OEt)_2$, but removal of the solvent by a stream of nitrogen and washing with light petroleum (b.p.40-60°C) was sufficient to cause rearrangement to $(PPh_3)_2PtS_2P(O)OEt$.

(OO'-Diethyldithiophosphato)bis(triphenylphosphine)platinum (II) tetraphenylborate. $Pt[S_2P(OEt)_2]_2$ in methanol was treated with an excess of triphenylphosphine in a minimum volume of acetone, followed by rapid addition of an aqueous solution of $NaBPh_4$. The white precipitate was well washed with water and diethyl ether, and dried *in vacuo* (40°C).

O-Ethyl Dithiocarbonate Complexes

Bis(O-ethyldithiocarbonato)platinum (II) was prepared from K_2PtCl_4 and KS_2COEt in aqueous solutions, as described in reference 66.

Bis(O-ethyldithiocarbonato)triphenylphosphine platinum (II) $Pt(S_2COEt)_2$ and PPh_3 (1:1 molar ratios) were shaken in a minimum volume of $CHCl_3$ to give a lemon-yellow solution. Trituration with an excess of light petroleum (b.p. 40-60°C) gave a pale yellow crystalline precipitate which was washed with diethyl ether and dried *in vacuo* (40°C). The same product (contaminated with a small amount of $(PPh_3)_2PtS_2CO$ was also obtained by reaction of $Pt(S_2COEt)_2$ with an excess of PPh_3 in CH_2Cl_2, followed by immediate addition of an excess of light petroleum (b.p. 40-60°C).

(Dithiocarbonate)bis(triphenylphosphine)platinum (II) chloroform. $Pt(S_2COEt)_2$ was shaken with an excess of PPh_3 in dichloromethane to give a colourless conducting solution. Partial removal of the solvent, and addition of light petroleum (b.p. 60-80°C) gave a white product which was non-conducting when redissolved in CH_2Cl_2 (m.p. 256°C)

(Found: C, 49.2; H, 3.3. Calculated for $C_{38}H_{31}Cl_3OP_2PtS_2$: C, 49.1; H, 3.3 %).

O-Ethyldithiocarbonato bis(triphenylphosphine)platinum (II) tetraphenylborate. $Pt(S_2COEt)_2$ in acetone-methanol was treated with an excess of PPh_3 in a minimum volume of acetone, followed immediately by addition of an aqueous solution of $NaBPh_4$. The resulting white precipitate was well washed with water and diethyl ether, and dried *in vacuo* (40°C).

TABLE 4.6

Analytical data for the platinum dithiocarbamate, xanthate and dithiophosphate compounds

Compound	m.p. (°C)	Found (°/o) C	H	N	Others	Required (°/o) C	H	N	Others
$Pt(S_2CNEt_2)_2PPh_3$	150-152	44.9	4.6	4.0	-	44.6	4.6	3.7	-
$Pt(S_2CNEt_2)_2PMePh_2$	163-165	40.2	4.7	4.4	-	39.9	4.8	4.1	-
$[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$	135-138	44.6	4.3	3.4	-	46.0	4.6	3.3	-
$[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$	132-133	48.5	5.2	3.5	S, 14.2	48.5	5.2	3.2	S, 14.4
$[Pt(S_2CNMe_2)(PPh_3)_2]Cl, H_2O$	196-197	51.8	4.2	2.4	-	52.4	4.3	1.6	-
$[Pt(S_2CNMe_2)(PPh_3)_2]BPh_4$	223-226	65.7	4.9	1.3	-	65.3	4.8	1.2	-
$[Pt(S_2CNMe_2)(PMePh_2)_2]Cl, H_2O$	120-124	45.3	4.3	2.3	Cl, 4.4	45.3	4.4	1.8	Cl, 4.6
$[Pt(S_2CNMe_2)(PMePh_2)_2]BPh_4$	198-203	61.5	5.0	1.5	-	61.5	5.0	1.4	-
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]Cl, 2H_2O$	109-111	34.7	4.6	2.5	Cl, 5.7	35.4	4.6	2.2	Cl, 5.5
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]BPh_4$	144-148	57.3	5.3	1.9	-	56.7	5.3	1.5	-
$[Pt(S_2CNEt_2)(PPh_3)_2]Cl, H_2O$	174-175	53.1	4.4	1.7	-	53.4	4.6	1.5	-
$[Pt(S_2CNEt_2)(PPh_3)_2]BPh_4$	94-97	66.2	5.1	1.4	-	65.8	5.1	1.2	-
$[Pt(S_2CNEt_2)(PMePh_2)_2]Cl, H_2O$	210-212	47.6	4.5	1.6	Cl, 4.5[a]	46.8	4.5	1.8	Cl, 4.5[a]

/...

Table 4.6 continued

Compound	m.p. (°C)	Found (%) C	H	N	Others	C	H	N	Others
$[Pt(S_2CNEt_2)(PMePh_2)_2]BPh_4$	169-171	62.4	5.2	1.3		62.2	5.3	1.3	-
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]Cl,H_2O$	99-100	38.9	5.2	2.2	Cl, 5.3	37.5	5.1	2.1	Cl, 5.3
$Pt\{S_2P(OEt)_2\}_2PPh_3$	97-101	38.1	4.2	-		37.7	4.2	-	-
$Pt[S_2P(O)OEt](PPh_3)_2$	227-230	51.2	4.0	-		52.1	4.0	-	-
$[Pt\{S_2P(OEt)_2\}(PPh_3)_2]BPh_4$	84-86	61.9	4.8	-		62.1	5.0	-	-
$Pt(S_2COEt)_2PPh_3$	164-169	42.5	3.4	-		41.4	3.6	-	-
$[Pt(S_2COEt)(PPh_3)_2]BPh_4$	86-90	65.4	5.0	-		65.2	4.8	-	-

[a] Found, O, 1.1. Required, 2.0 %.

CHAPTER 5

Crystal structure of Bis(diethyldithiocarbamato) triphenylphosphine-platinum(II)

CHAPTER 5

The Crystal Structure of bis(diethyldithiocarbamato)triphenylphosphineplatinum (II).

$Pt(S_2CNEt_2)_2PPh_3$ was prepared as described in Chapter 4, and was found to form bright yellow almost tetragonal prismatic crystals. Ni-filtered Cu-Kα X-radiation was used throughout the structure determination.

5.1 Preliminary Cell Dimensions and Space Group

The oscillation and zero-layer Weissenberg photographs of one of the crystals mounted along the needle axis (b) showed that the crystal was monoclinic with this axis unique. On the Weissenberg film, the other two axes were found to be very nearly 90° apart, thus making the crystal almost orthorhombic. The absences on the zero-layer Weissenberg (absent hOl where h+l=odd) indicated an n-glide perpendicular to b, and the absences in OkO (absent where k=odd), shown in a precession photograph of the crystal mounted along b, indicated a two-fold screw along this axis. The space group was therefore $P2_1/n$ (alternative setting of $P2_1/c$, No. 14).

Approximate cell dimensions were obtained for b from the oscillation photograph (9.931 Å), and for the reciprocal cell dimensions a*(0.0538 $Å^{-1}$), c*(0.0620 $Å^{-1}$) and β*(89.6°) from the axial rows of the zero-layer Weissenberg film. The corresponding direct cell parameters a, c and β were obtained by calculation.

The crystal density was found by flotation in a potassium

TABLE 5.1

2θ values obtained from α_1, α_2 splittings

h	k	l	Splitting[a]	2θ(obs)	Error[b]	2θ(calc)
6	O	-2O	O.8O	16O.14	±2.O	16O.363
6	O	2O	O.85	161.29	±1.5	16O.636
9	O	-19	O.65	155.68	±2.5	156.396
12	O	-18	1.OO	164.O5	±1.3	164.O75
12	O	18	1.2O	166.68	±O.8	167.O71
18	O	-14	2.O5	172.17	±O.3	172.867
22	O	-8	O.75	158.85	±2.O	16O.OO5
22	O	8	O.9O	162.3O	±1.5	161.868
24	O	O	1.1O	165.48	±1.O	165.4O5
24	O	2	1.45	168.96	±O.5	17O.895
6	1	-2O	O.9O	162.36	±1.5	162.518
9	1	-19	O.75	158.91	±2.O	158.173
15	1	-16	O.85	161.34	±1.5	16O.O11
15	1	16	O.97	163.69	±1.3	162.599
21	1	-1O	1.1O	165.53	±1.3	165.421
23	1	-6	1.45	168.99	±O.5	168.239
23	1	-5	O.75	158.91	±2.O	158.369
23	1	5	O.8O	16O.2O	±2.O	159.474
24	1	O	1.43	168.77	±O.5	168.437
16	2	-15	O.83	16O.94	±2.O	16O.11O
16	2	15	O.93	162.97	±1.3	162.712
18	2	13	O.8O	16O.28	±2.O	158.717

Table 5.1 page 2

h	k	l	Splitting[a]	2Θ(obs)	Error[b]	2Θ(Calc)
20	2	-11	0.90	162.52	±1.5	163.544
20	2	11	1.20	166.84	±0.8	166.485
22	2	7	0.80	160.38	±2.0	158.315
1	3	20	0.75	159.43	±2.0	159.109
2	3	-20	0.80	160.69	±2.0	160.510
3	3	-20	0.95	163.69	±1.3	163.573
3	3	20	1.05	165.22	±1.0	164.323
4	3	-20	1.35	168.47	±0.6	169.262
8	3	-19	1.00	164.49	±1.3	164.151
17	3	-14	1.43	169.07	±0.5	168.781
21	3	-9	1.40	168.88	±0.6	167.868
21	3	9	1.80	171.34	±0.4	171.520
22	3	-7	1.45	169.27	±0.5	168.469
22	3	-6	0.75	159.43	±2.0	157.109
23	3	-4	1.65	170.56	±0.4	170.085
23	3	0	0.67	157.37	±0.6	156.197
23	3	2	0.80	160.69	±2.0	159.155
23	3	3	1.00	164.49	±1.3	163.340
1	5	-19	0.85	162.76	±1.5	161.261
1	5	19	0.85	162.76	±1.5	161.466
3	5	-19	1.20	167.72	±0.8	166.699
3	5	19	1.25	168.21	±0.7	167.585
22	5	1	0.93	164.07	±1.3	163.340
22	5	2	1.03	165.55	±1.0	166.497

Table 5.1 page 3

h	k	l	Splitting[a]	2Θ(obs)	Error[b]	2Θ(calc)
8	6	17	1.10	167.16	±1.0	166.064
12	6	-15	0.85	163.45	±1.5	160.516
14	6	-14	1.65	171.40	±0.4	171.030
16	6	-12	0.95	165.16	±1.3	162.928
17	6	11	1.00	165.89	±1.3	167.241
20	6	-6	1.00	165.89	±1.0	163.330
20	6	6	1.20	168.21	±0.8	164.842
20	7	1	0.90	161.31	±1.5	163.416
17	9	1	0.97	163.25	±1.3	164.219
15	10	2	1.45	169.01	±0.5	170.149
12	11	2	1.00	164.13	±1.3	163.705
8	12	1	0.90	162.33	±1.5	161.406

[a] ±0.07 mm. [b] The errors in 2Θ were calculated by including the errors in the splitting (±0.07 mm), in the camera diameter (±0.1mm), and in ζ (±0.015 $Å^{-1}$)

TABLE 5.2

Crystal data for $Pt(S_2CNEt_2)_2PPh_3$

Crystal System	monoclinic
Space Group	$P2_{1/n}$, Z = 4
Cell Dimensions	a = 18.6527(37) Å
	b = 9.9625(69) Å
	c = 16.1517(58) Å
	$\alpha = 90^\circ$
	$\beta = 90.219(22)^\circ$
	$\gamma = 90^\circ$
Cell Volume	V = 3001.43 $Å^3$
Density	do = 1.65 g cm^{-3}
	dc = 1.67 g cm^{-3}
Linear Absorption Coefficient	μ = 121.429

iodide-water solution since the crystals were soluble in all organic solvents. The observed density of 1.65 g cm^{-3} was consistent with that calculated for four molecules in the unit cell (1.67 g cm^{-3}).

5.2 Accurate Cell Dimensions

All the Weissenberg films showed reflections out to highest Θ values, with many widely spaces α_1, α_2 reflections near the edge of the film. Measurement of the splitting of the reflections hkl (k=O→ 6); hkl (l=O, 1, 2) allowed accurate values of Θ to be obtained. These values were weighted according to the calculated errors, and used in a least squares refinement of the cell dimensions. The error due to the camera radius was minimised by careful measurement of the camera diameter and film thickness. Only reflections whose splitting was greater than O.7 mm were included in the refinement, since the error in every splitting measurement was at least O.O7 mm. For measurements obtained from upper layer Weissenberg films, a further error due to the error in ζ was included. Table 5.1 lists the reflections used and Table 5.2 lists the final values obtained.

5.3 Three Dimensional Intensity Data

The planes hkl (h=O→ $\pm$ 25, k=O→ 6, l=O→ $\pm$ 22) were obtained from equi-inclination Weissenberg photographs of a crystal oscillating about b, giving a total of 3392 independent reflections, out to a maximum of 2Θ value of 169.9°. A second crystal mounted along c allowed the additional planes hkl (h=O→ $\pm$ 25, k=O→ $\pm$14, l=O→ 3) to be collected, giving a further 491 independent reflections which were used as supplementary data in the final refinement of the

structure. Intensity estimation of the data was made by the SAAB scanner, linked to a PDP 15 computer. The data was then corrected for Lorentz and polarisation effects[67].

The high linear absorption coefficient indicated the necessity for absorption correction of the data. The overall dimensions of the first crystal were 0.4 x 0.16 x 0.32 mm with the crystal mounted along the longest dimension, but the cross-section was of irregular shape. An approximate correction was made by treating it as a cylinder of radius 0.08 mm[69]. The second crystal more nearly resembled a sphere of radius 0.15 mm and the data was corrected accordingly[69].

5.4 Accuracy of the Data

The use of the PDP 15 computer with the SAAB scanner allowed the full scan record to be stored which gave a greater possibility for accurate intensity measurement, since no estimations for missing density data had to be made (cf. previous structure), and the background transmission near each spot could be considered. The widely separated α_1, α_2 reflections were, however, still missed as they lay too far outside the positions calculated by the program (which used the Cu Kα-wavelength).

Comparison of the observed and calculated structure factors found for this structure during the final stages of refinement, showed greatest disagreement for reflections of very weak and very high scanned intensities, and suggested that the range of accuracy in the scanner intensities was less than had originally been assumed.

Similar results were shown in the intensities of other compounds, scanned by this process [87], and a preliminary comparison of intensities obtained by this scan process and by diffractometer has also indicated least accuracy in these regions [88].

Since several of these reflections were used to scale films of different exposure times, this would be expected to result in particularly inaccurate values of the extremely intense spots, whose intensities were only measurable on the shortest exposure films, and were then scaled up. The platinum position in the unit cell for this structure (see section 5.5) added to the likely inaccuracies. Almost all the reflections to which the Pt contributed were very strong, while the other reflections to which only the other atoms contributed were very weak, and were generally only obtainable on the longest exposure film. Very few reflections of intermediate intensity were thus available for scaling between this film and films of shorter exposure. The observations on the range of scanner accuracy now suggest that separate treatment of the two reflection categories might have been worthwhile.

5.5 Refinement of the Structure

The reflections on the Weissenberg films showed considerable contrast in intensity. The Pt and possibly the other heavy atoms contributed to the very strong spots which extended out to highest θ values. The spots to which the other atoms contributed chiefly were very much weaker and ranged only to medium θ values. In addition, the strongest spots showed higher symmetry than that of the original

space group. Pseudo orthorhombic behaviour was shown by the great similarity of F_{hkl} and $F_{hk\bar{l}}$, and the conditions for these reflections (present for hOl where l=even; and for hkl where h+k=even) implied the pseudo-space group Cmcm for the platinum atom, occupying the special four-fold positions $(O, y, \frac{1}{4}; O, \bar{y}, \frac{3}{4}; \frac{1}{2}, \frac{1}{2}+y, \frac{1}{4}; \frac{1}{2}, \frac{1}{2}-y, \frac{3}{4})$.

Using the data (without correction for absorption) obtained from the first crystal, a Patterson vector map was calculated and used to determine the heavy atom position. The space group $P2_1/n$ for the cell infers four equivalent positions for the Pt atom at $(x, y, z; \bar{x}, \bar{y}, z; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$. In the Patterson vector map the Pt-Pt vectors from these positions appeared as peaks at u, v, w $(=2x, 2y, 2z)$, Harker lines at $\frac{1}{2}, \frac{1}{2}\pm v, \frac{1}{2}$ and Harker planes at $\frac{1}{2}-u, \frac{1}{2}, \frac{1}{2}-w$ and $\frac{1}{2}+u, \frac{1}{2}, \frac{1}{2}+w$, in addition to the major peak at the origin. The atomic coordinates obtained for Pt$(O, O.137, O.25)$ were in agreement with the higher space group suggested for the platinum atom.

A difference Fourier, using the Pt as phasing model, enabled the position of four of the heavy atoms to be obtained. The calculated R factor with only the Pt contribution was O.59. Average scattering factors for the sulphur and phosphorus atoms were used in a further difference Fourier map to obtain the fifth heavy atom. Least squares refinement reduced the R factor to O.27. From a further difference Fourier, the positions of two phenyl rings, and one C-N group were found, which distinguished the heavy atom types. The remaining phenyl ring, C-N group and finally the ethyl groups were found from

successive difference Fourier maps.

The carbons in each phenyl ring were moved to form an idealised phenyl ring in the best plane of the original ring but were not constrained to remain in the idealised ring. Full matrix least squares refinement of all the atoms isotropically reduced the calculated R factor to O.19. Correction of the data for absorption effects, followed by successive least squares refinement using only the reflections with a scanned intensity above 15O, further reduced the R factor to O.11. A weighting factor w (w=1 for $F_o \leqslant A$, $w=\frac{A}{F_o}^2$ for $F_o > A$ was used, where A=14O on the scale of Table 5.7 . After absorption corrected data obtained from the second crystal was included, further refinement of the structure with the heavy atoms anisotropic gave a final R factor of O.1O.

The fractional coordinates and thermal parameters for each atom are given in Table 5.3. A projection of the structure is shown in Figure 5.1 which also shows the labelling of all the atoms and the thermal ellipsoids of the heavy atoms. Figure 5.2 shows a b-axis projection of the unit cell.

TABLE 5.3

Fractional coordinates of atoms and thermal parameters (x 100) ($Å^2$) for $Pt(S_2CNEt_2)_2PPh_3$

	x	y	z	U
Pt	0.0014(1)	0.1416(1)	0.2469(1)	
P	-0.0830(4)	0.2696(7)	0.3062(5)	
S1	0.0900(4)	0.2377(8)	0.3297(5)	
S2	0.1337(6)	0.3413(12)	0.1633(6)	
S3	-0.0744(5)	0.0152(8)	0.1660(7)	
S4	0.0749(5)	-0.0128(9)	0.1792(6)	
C1	0.1346(16)	0.3483(31)	0.2664(20)	2.8(7)
C2	-0.0006(14)	-0.0555(28)	0.1274(18)	2.3(6)
C3	0.2281(20)	0.5366(42)	0.2581(26)	5.0(9)
C4	0.1948(29)	0.6756(56)	0.2361(35)	8.3(15)
C5	0.1720(23)	0.4704(49)	0.3953(29)	6.4(12)
C6	0.2316(22)	0.3931(42)	0.4471(28)	5.8(11)
C7	-0.1626(15)	0.2858(29)	0.2449(19)	2.4(6)
C8	-0.1714(22)	0.3804(40)	0.1908(28)	5.3(10)
C9	-0.2312(27)	0.3966(54)	0.1328(34)	7.6(14)
C10	-0.2826(23)	0.2924(46)	0.1406(28)	5.9(11)
C11	-0.2758(24)	0.1878(49)	0.1914(31)	6.6(12)
C12	-0.2126(22)	0.1744(42)	0.2453(27)	5.3(10)
C13	-0.1168(19)	0.2027(36)	0.4004(23)	4.2(8)
C14	-0.0816(18)	0.0914(38)	0.4349(23)	4.1(8)
C15	-0.1021(18)	0.0245(40)	0.5061(24)	4.4(9)

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	x	y	z	U
C16	-0.1606(21)	0.0680(43)	0.5487(27)	5.4(10)
C17	-0.1986(20)	0.1830(37)	0.5171(24)	4.4(9)
C18	-0.1726(18)	0.2440(36)	0.4448(23)	4.2(8)
C19	-0.0549(13)	0.4367(26)	0.3310(17)	1.7(5)
C20	-0.0639(16)	0.4997(31)	0.4080(20)	3.0(7)
C21	-0.0420(23)	0.6357(41)	0.4191(27)	5.4(10)
C22	-0.0096(16)	0.7106(35)	0.3580(21)	3.4(7)
C23	-0.0000(17)	0.6582(33)	0.2927(21)	3.7(7)
C24	-0.0321(14)	0.5186(29)	0.2732(18)	2.4(6)
C25	0.0571(34)	-0.1999(70)	0.0327(41)	10.0(19)
C26	0.0683(31)	-0.3630(56)	0.0222(38)	8.5(16)
C27	0.0700(18)	-0.1914(36)	0.0278(23)	4.1(8)
C28	0.1142(29)	-0.2934(58)	0.0754(35)	8.1(15)
N1	0.1781(13)	0.4405(25)	0.3042(16)	3.1(6)
N2	-0.0000(14)	-0.1498(27)	0.0703(17)	3.5(6)

Anistropic Temperature Factors (x 100)

	U11	U22	U33	U12	U13	U23
Pt	3.3(1)	3.1(1)	2.8(1)	-0.3(1)	0.4(0)	-0.1(1)
P	2.8(4)	1.8(3)	2.0(4)	-0.1(3)	-0.4(3)	0.2(4)
S1	2.5(3)	4.2(4)	2.1(4)	-0.8(3)	0.2(3)	0.4(5)
S2	5.4(5)	7.0(7)	3.0(5)	-2.1(5)	0.5(4)	-0.1(6)
S3	4.1(4)	2.5(3)	5.6(6)	0.6(3)	-1.4(4)	-2.2(6)
S4	4.1(5)	4.3(5)	4.6(5)	-0.0(4)	0.9(4)	-2.2(6)

Projection of the molecule $Pt(S_2CNEt_2)_2PPh_3$

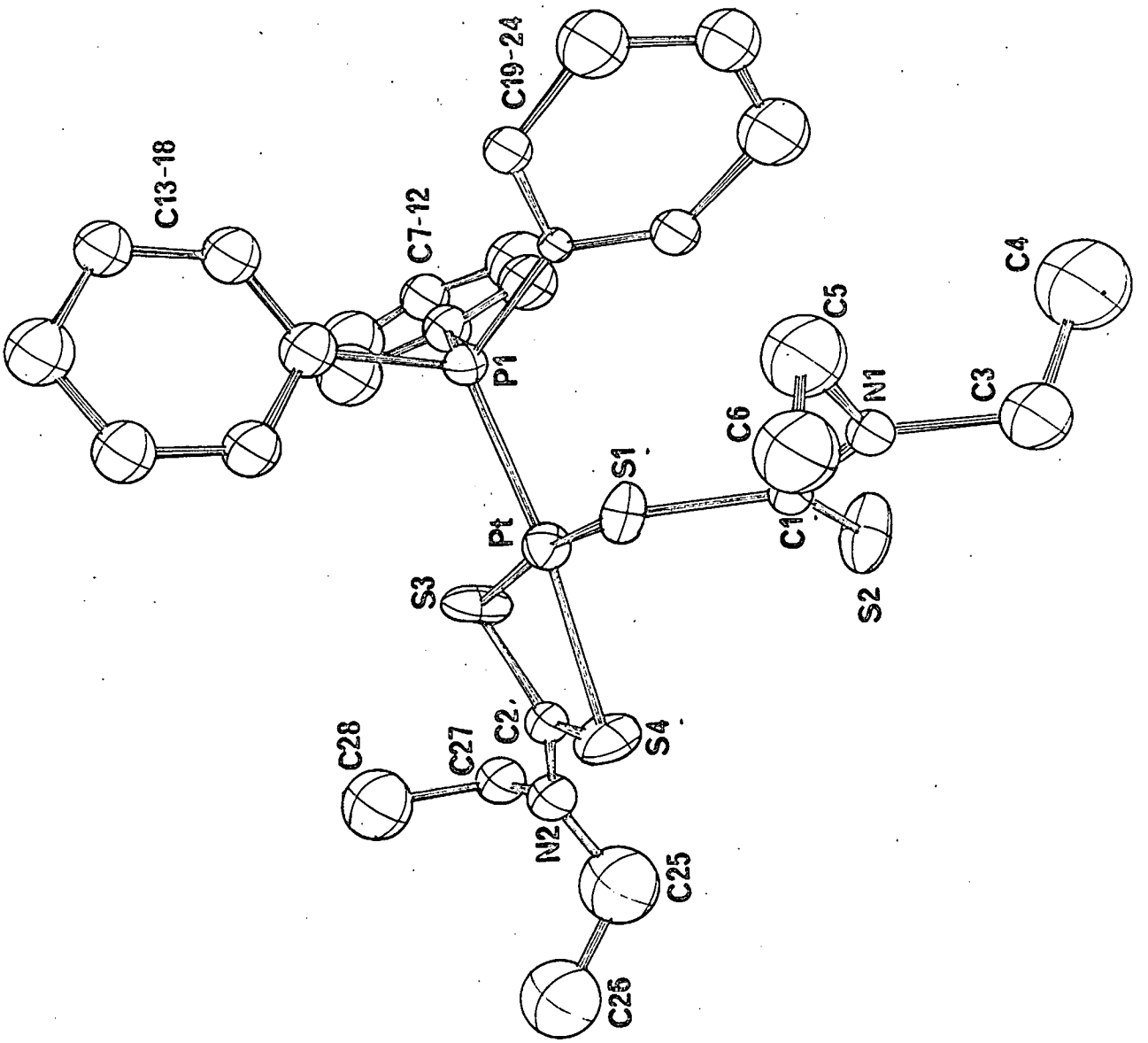

Figure 5.1

b-axis projection of the unit cell of $Pt(S_2CNEt_2)_2PPh_3$

centred about the point $(\frac{1}{2}, 0, \frac{1}{2})$

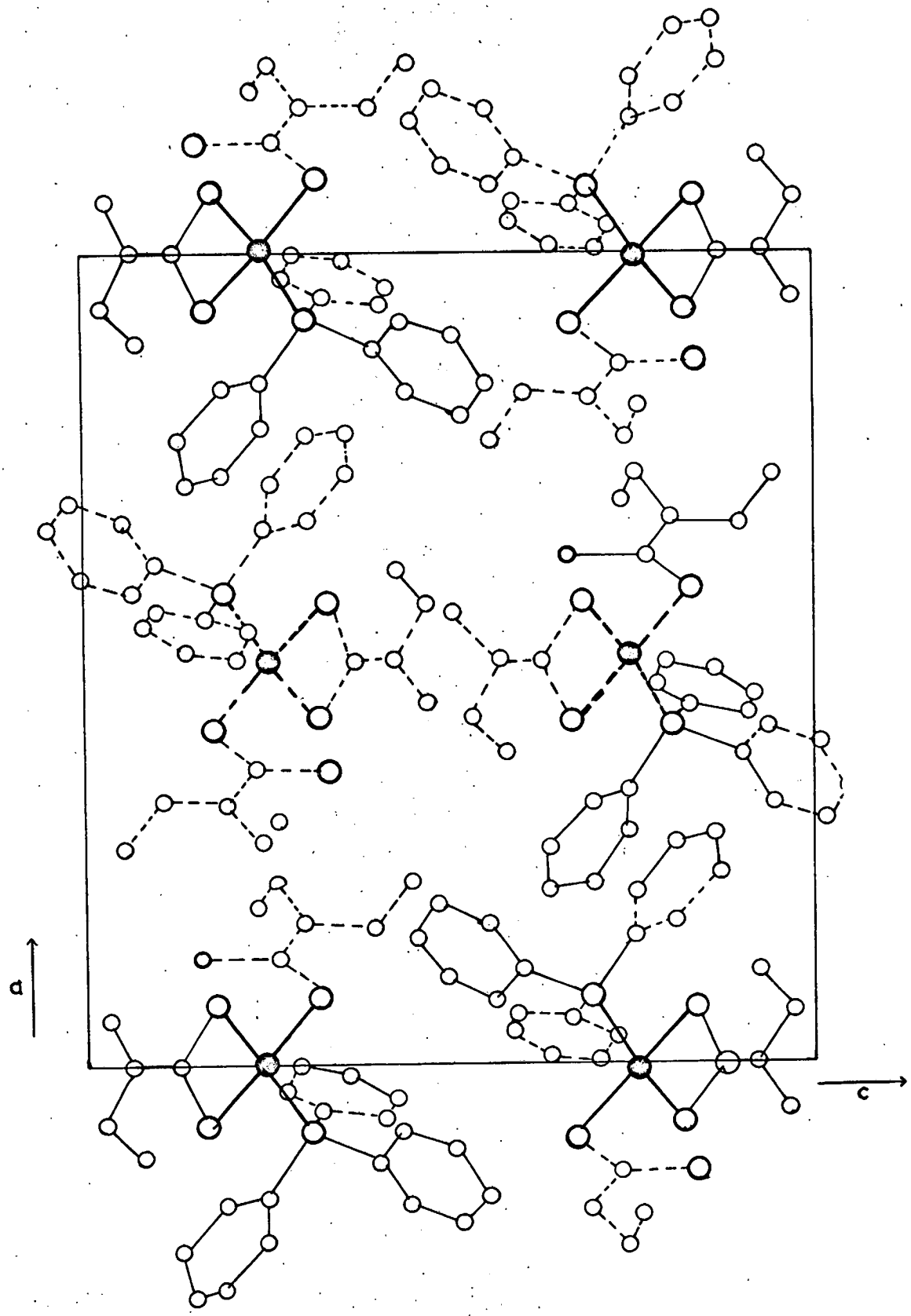

Figure 5.2

TABLE 5.4

Bond distances in Å for $Pt(S_2CNEt_2)_2PPh_3$

Pt-S1	2.328(9)
Pt-S2	3.449(12)
Pt-S3	2.298(10)
Pt-S4	2.335(10)
Pt-P	2.243(8)

Monodentate Ligand		Bidentate Ligand	
S1-C1	1.720(32)	S3-C2	1.669(29)
S2-C1	1.667(33)	S4-C2	1.689(29)
C1-N1	1.367(39)	C2-N2	1.317(40)
N1-C3	1.532(48)	N2-C25	1.325(70)
N1-C5	1.506(54)	N2-C27	1.529(44)
C3-C4	1.558(69)	C25-C26	1.647(90)
C5-C6	1.589(63)	C27-C28	1.520(67)

Phosphine Distances

P-C7	1.789(29)	C15-C16	1.363(54)
P-C13	1.779(38)	C16-C17	1.439(56)
P-C19	1.791(27)	C17-C18	1.405(53)
C7-C8	1.296(52)	C18-C13	1.330(51)
C8-C9	1.462(68)	C19-C20	1.403(42)
C9-C10	1.419(69)	C20-C21	1.426(52)

C10-C11	1.332(67)	C21-C22	1.378(55)
C11-C12	1.468(63)	C22-C23	1.191(48)
C12-C7	1.449(50)	C23-C24	1.546(44)
C13-C14	1.403(52)	C24-C19	1.312(39)
C14-C15	1.384(54)		

TABLE 5.5

Bond angles in degrees for $Pt(S_2CNEt_2)_2PPh_3$

About the metal atom

S3-Pt-S4	74.5(3)	Pt-S3-C2	86.4(10)
S3-Pt-P	97.1(3)	Pt-S4-C2	84.8(10)
S1-Pt-P	91.1(3)	Pt-S1-C1	105.4(11)
S1-Pt-S4	97.1(3)	Pt-P-C7	113.4(10)
S1-Pt-S3	170.4(3)	Pt-P-C13	113.9(12)
S4-Pt-P	171.3(3)	Pt-P-C19	114.8(9)

Monodentate ligand		Bidentate ligand	
S1-C1-S2	124.3(19)	S3-C2-S4	113.3(17)
S1-C1-N1	116.9(23)	S3-C2-N2	124.9(22)
S2-C1-N1	118.5(23)	S4-C2-N2	121.2(21)
C1-N1-C3	124.3(27)	C2-N2-C25	126.8(37)
C1-N1-C5	121.4(28)	C2-N2-C27	119.9(25)
C3-N1-C5	113.6(28)	C25-N2-C27	112.2(36)
N1-C3-C4	115.1(33)	N2-C25-C26	121.4(51)
N1-C5-C6	111.3(34)	N2-C27-C28	114.7(33)

Phosphine Angles

C7-P-C13	102.1(15)	C13-C14-C15	125.5(34)
C7-P-C19	106.4(13)	C14-C15-C16	119.3(36)
C13-P-C19	105.1(15)	C15-C16-C17	117.9(37)
P-C7-C8	122.8(26)	C16-C17-C18	117.9(34)
P-C7-C12	117.5(24)	C17-C18-C13	126.0(34)
C8-C7-C12	118.7(32)		

C7-C8-C9	127.4(39)	P-C19-C2O	125.3(21)
C8-C9-C1O	112.1(43)	P-C19-C24	12O.9(22)
C9-C1O-C11	124.4(43)	C2O-C19-C24	113.1(26)
C1O-C11-C12	12O.7(42)	C19-C2O-C21	12O.1(3O)
C11-C12-C7	116.3(36)	C2O-C21-C22	123.4(37)
		C21-C22-C23	117.6(36)
P-C13-C14	118.O(27)	C22-C23-C24	121.O(31)
P-C13-C18	128.7(29)	C23-C24-C19	122.7(27)
C14-C13-C18	113.3(34)		

5.6 Discussion of the Structure

In bis(NN-diethyldithiocarbamato)triphenylphosphineplatinum (II) the platinum atom is four coordinate in the solid state as shown in Figure 5.1. The platinum is coordinated to both sulphur atoms of one dithiocarbamate ligand, and to one sulphur of the other ligand. The fourth coordinate bond is to the phosphorus of the triphenyl phosphine. The remaining sulphur atom of the monodentate dithiocarbamate ligand is not bonded to the platinum. Thus, the coordination around the metal atom in this complex, in the solid state, is closely similar to the previous structure in Chapter 3.

All the platinum-sulphur bond distances fall within the range 2.34-2.29 Å similar to those found in $Pt(S_2CNEt_2)_2$ (2.29-2.32 Å [90]) and in Pt(p-dithiocumato)$_2$PPh$_2$Me (2.30-2.39 Å [70]). The platinum-sulphur bonds cis to the phosphine group in $Pt(S_2CNEt_2)_2PPh_3$ are slightly shorter at 2.328(9) and 2.298(10) Å than the platinum-sulphur bond trans to the phosphine (2.335(10) Å) although the significant error in all these bond lengths may make a comparison of this sort of little value. The platinum-phosphorus bond distance of 2.243(8) Å is close to that found in Pt(p-dithiocumato)$_2$PPh$_2$Me (2.245(3) Å [70]) where platinum-phosphorus π-interaction was postulated from the bond length. In the latter compound definite lengthening of the platinum-sulphur bond trans to the phosphine was observed (2.39 Å).

The platinum atom, and the four atoms coordinated to it are very close to planar. The slight deviation from planarity is chiefly due to the platinum atom which is slightly displaced (0.075 Å) from

a plane containing the four cooordinated atoms. Table 5.6 lists the planes for these atoms and some other least squares planes for the molecule.

The non-bonded platinum-sulphur distance is 3.449(12) Å. This distance is shorter than the palladium-sulphur contact distances quoted for bis(dithiobenzoato)palladium (3.46 Å[71]) but there the sulphur atoms are situated so that interaction with the metal d_z orbitals is possible. In $Pt(S_2CNEt_2)_2PPh_3$ the free sulphur atom lies 2.726 Å perpendicularly above the plane of the $PtPS^1S^3S^4$ group at a projected distance of 2.188 Å from the platinum atom, and thus it is not near an apical position of a square pyramid.

The geometry around the platinum atom is distorted from square planar as the angles, listed in Table 5.5, deviate considerably from 90°. This distortion is chiefly due to the S-Pt-S angle of 74.5(3)° caused by the four membered chelate ring, which is close to the S-Pt-S angle of 75.5° found in $Pt(S_2CNEt_2)_2$[90].

A least squares plane calculated for the S_2CN group of the bidentate ligand shows that the ligand is planar. The platinum atom, and the ethyl carbon atoms which are bonded to the nitrogen lie close to this plane (0.216 Å and 0.032, 0.149 Å from it respectively). The carbon-sulphur bond distances (1.669(29), 1.689(29) Å) are slightly shorter than those obtained in $Ni(S_2CNEt_2)_2$[91] or $Pt(S_2CNEt_2)_2$[90] but are within the range found in bis(dithiobenzoato)palladium[71] and other dithiolato chelate complexes[4,5,6]. These bond distances are intermediate between the carbon-sulphur single bond length (1.81 Å[74])

and double bond length (1.61 Å [74]). The carbon-nitrogen bond is 1.317 Å and is close to that found in $Pt(S_2CNEt_2)_2$ (1.308 Å [90]). This bond also shows partial double bond character being intermediate between the single and double bond lengths (1.475, 1.28 Å respectively [74]). Thus extensive electron delocalisation throughout the S_2CN moiety of the bidentate ligand is indicated, as has been inferred in many other chelate dithiocarbamate metal complexes [4,5]. The S-C-S angle (113.3°) is close to that found in $Ni(S_2CNEt_2)_2$ [91] and $Au(S_2CNEt_2)_3$ [72] and the remaining bond distances and angles are close to those previously reported in all dithiocarbamate chelate complexes.

In the monodentate ligand the S_2CNC_2 group is again almost planar (Table 5.6) but the platinum atom is 0.657 Å from this plane. There is a significant difference between the two carbon-sulphur bonds. The carbon-sulphur bond distance of the uncoordinated sulphur is definitely shorter (1.667(33) Å) than the coordinated sulphur-carbon bond distance (1.720(32) Å) but the length of the latter bond indicates that some double bond character is still present, as has been observed in the carbon-sulphur bonds of the monodentate ligands in $Au(S_2CNEt_2)_3$ [72] and Pt(p-dithiocumato)$_2$PPh$_2$Me [70]. The carbon-nitrogen bond is considerably longer (1.367(39) Å) than that obtained in the chelate ligand, consistent with the decreased electron delocalisation over the S_2CN moiety but the bond distance is still shorter than the carbon-nitrogen single bond length (1.475 Å [74]).

The S-C-S angle is increased in the monodentate ligand from 113.3(17)° to 124.3(19)° and the Pt-S-C angle is increased to 105.4(11)°

from 85(1)°. The sulphur-sulphur 'bite' distance is lengthened to 2.995(13) Å in the monodentate ligand compared with 2.805(13) Å in the bidentate ligand. The remaining bond angles and distances are close to those previously reported for dithiocarbamate complexes.

All the phenyl rings of the phosphine are planar, although the rings are poorly resolved. Carbon-carbon distances range from 1.19(5) Å to 1.55(4) Å, and the ring angles vary from 112(4) to 129(3)°.

TABLE 5.6

Some least squares planes for $Pt(S_2CNEt_2)_2PPh_3$

The table shows the equation of the plane[a], and distances of the atoms from the plane[b]. Atoms marked * were not included in the plane calculation.

PLANE 1

P = -2.6051 Q = -6.7183

R = 11.7198 S = 2.0134

P	-0.020
S1	0.019
S3	0.023
S4	-0.023
*Pt	-0.075
*S2	-2.741
*Cl	-1.582
*C2	-0.146
*N1	-1.872
*N2	-0.183

σ = 0.023

PLANE 2

P = -2.6076 Q = 6.7137

R = 11.7263 S = 2.0006

Pt	-0.060
P	-0.004
S1	0.035
S3	0.037
S4	-0.009
*S2	-2.726
*Cl	-1.566
*C2	-0.132
*N1	-1.855
*N2	-0.171

σ = 0.040

PLANE 3

P = -2.3323 Q = -7.3271

R = 10.7634 S = 1.8325

S3	0.016
S4	0.015
C2	-0.053

PLANE 4

P = 14.4645 Q = -6.2901

R = -0.1276 S = -0.2452

S2	0.011
S1	0.010
C1	-0.033

Table 5.6 page 2

PLANE 3

N2	0.022
*Pt	-0.216
*C25	-0.149
*C27	0.032

σ = 0.035

PLANE 4

N1	0.012
*Pt	-0.657
*C3	0.136
*C5	-0.277

σ = 0.022

PLANE 5

P = -9.1567 Q = 5.0273

R = 11.5011 S = 5.6688

P	-0.032
C7	0.073
C8	0.007
C9	-0.030
C10	0.006
C11	0.001
C12	-0.024

σ = 0.036

PLANE 6

P = 11.0039 Q = 6.0440

R = 8.5700 S = 3.3630

P	-0.023
C13	0.008
C14	0.019
C15	-0.001
C16	-0.017
C17	-0.010
C18	0.024

σ = 0.018

PLANE 7

P = 16.8667 Q = -3.3256

R = 4.2450 S = -1.0110

P	0.015
C19	0.039
C20	0.003

Table 5.6 page 3

C21	-0.032
C22	0.005
C23	0.065
C24	-0.095

σ = 0.052

[a] The form of the plane equation is Px+Qy+Rz = S in cartesian coordinates, where x, y and z are the fractional coordinates of the atoms in the direct cell.

[b] in Å.

TABLE 5.7 page 1

Structure factors (F_{obs}, F_{calc}) for $Pt(S_2CNEt_2)_2PPh_3$

0,0,L			6,0,L			-1	111*	107	8	914	962	18	597	-531
						1	478	-473				19	383	421
6	1162	-1341	-18	893	-730	3	703	531	10,0,L					
8	802	1083	-16	1025	928	5	299	-364				2,1,L		
10	1612	-2080	-14	883	-797	7	455	-435	-11	69*	-245			
12	1702	2284	-12	873	897	17	88*	175	-7	519	-635	-19	251*	-273
14	1394	-1751	-10	1551	-1865				-3	175*	-186	-18	179*	-217
16	1053	1205	-8	1842	2345	12,0,L			-1	118*	-86	-17	443	397
18	735	-737	-6	2126	-3127				1	293*	-11	-16	237*	59
			-4	1766	2748	-16	925	1118	3	251	319	-15	43*	-439
1,0,L			-2	1592	-2160	-14	1122	-1192	9	93*	327	-13	326*	340
			0	1223	1429	-12	670	712				-12	994	-1005
-17	176*	146	2	2192	-2458	-10	719	-680	20,0,L			-11	125*	48
-15	353	-512	4	2148	2504	-9	348*	0				-10	859	829
-13	613	763	6	2753	-3023	-8	479	542	-10	579	-742	-9	239*	-238
-11	552	-626	8	2360	2887	-6	1050	-1135	-8	797	1011	-8	545	-522
-9	290*	105	10	1555	-1821	-4	1453	1842	-6	907	-1017	-7	325*	64
-7	806	813	12	885	956	-2	1824	-2368	-4	834	818	-6	714	-591
3	501	416	14	692	-681	0	2071	2770	-2	514	-552	-5	587	511
5	221*	118	16	844	866	2	1600	-1722	0	460	512	-4	977	935
7	142*	-32	18	702	-909	4	1110	1115	2	508	-629	-3	999	-1228
9	384	-370				6	877	-868	4	696	769	-1	933	690
13	187*	182	7,0,L			8	803	772	6	685	-688	3	1598	-1218
15	429	-529				10	1147	-1312	8	619	740	4	742	631
19	791	-540	-15	193*	-272	12	1111	1217				5	101*	141
			-13	199*	237	14	1041	-943	21,0,L			6	628	-463
2,0,L			-11	480	368	16	1224	956				7	186*	-133
			-7	633	-711	18	631	-593	-9	274	340	8	693	635
-18	688	-864	-5	260	303				-1	177*	-44	9	151*	204
-16	1179	1108	-3	314	-345	13,0,L			1	171*	-109	10	86*	-31
-14	1274	-1472	-1	171*	124				3	293	313	11	423	-312
-12	1445	1903	1	639	547	-3	249*	-142	7	49*	-103	13	89*	287
-10	1502	-1889	3	666	-639	-1	297	376				14	206*	-229
-8	1030	1361	5	147*	-200	1	290*	88	22,0,L			15	283*	-198
-6	1186	-1701	7	291*	-188	5	376*	121				16	531	542
-4	1194	1874	11	345	-450				-6	501	-630	17	149*	96
6	1368	-1776	13	273	474	14,0,L			-2	746	-867	18	416	-407
8	1269	1598	17	43*	61				0	752	875	19	232*	-284
10	1151	-1317				-14	1054	-1256	2	632	-764			
12	1377	1611	8,0,L			-12	1095	1155	4	508	520	3,1,L		
14	949	-1048				-10	949	-1002	6	306	-320			
16	657	805	-14	187	-234	-8	719	713	8	96*	297	-19	684	-566
18	961	-654	-12	941	924	-6	621	-724				-18	484	-435
			-10	1611	-1943	-4	1169	1298	23,0,L			-17	1012	922
3,0,L			-8	2335	2836	-2	1748	-2141				-16	834	788
			-6	2043	-2774	0	1760	2282	-3	108*	-59	-15	1234	-1159
-17	154*	256	-4	1519	1938	2	1352	-1456	-1	180	249	-14	1148	-1143
-15	210	-310	-2	1614	-1955	4	1118	1078	1	287	-352	-13	1238	1268
-13	286	375	0	1251	1484	6	961	-968				-12	1185	1120
-11	531	-680	2	1941	-2303	8	1131	1193	0,1,L			-11	974	-1054
-9	692	841	4	1694	1684	10	1238	-1350				-10	1174	-1177
-7	75*	-22	6	1910	-2210				4	891	773	-9	1398	1422
-3	451*	169	8	1556	1593	15,0,L			5	564	538	-8	772	915
-1	576	955	10	1333	-1594				6	875	700	-7	1259	-1498
1	852	1017	12	1263	1407	-5	479	475	7	709	-692	-6	1074	-1215
3	1329	1300	16	975	1032	-3	438	-446	8	253*	85	-5	1537	1883
5	1035	912				-1	463	582	9	93*	68	-4	1961	1421
7	708	-741	9,0,L			1	241*	467	10	813	-629	-3	1403	-1763
9	331*	-76				3	395	-444	11	260*	25	-2	2097	-3168
11	259*	-99	-13	117*	273	5	307	258	12	584	648	2	1964	-1538
13	242	-199	-11	613	-584	9	257	-374	13	294*	143	3	3124	2796
15	163*	-54	-9	399	386				14	607	-503	4	1298	1082
			-7	498	-584	16,0,L			15	339	-375	5	2218	-1907
4,0,L			-5	367	-332				16	204*	145	6	1594	-1455
			-1	323	313	-14	676	-828	17	380	303	7	2185	2162
-18	1116	-938	1	224*	-302	-12	833	901	19	203*	-326	8	1605	1480
-16	1245	1298	3	337*	211	-10	938	-1012				9	1659	-1569
-14	1081	-1179	5	775	-718	-8	928	1003	1,1,L			10	1196	-1140
-12	1204	1369	7	909	-590	-6	895	-958				11	1017	975
-10	1402	-1829				-4	739	758	-19	693	-614	12	860	890
-8	1574	2044	10,0,L			-2	789	-842	-18	433	-406	13	721	-732
-6	1679	-2408				0	1175	1312	-17	773	701	14	564	-599
-4	1721	2818	-16	1141	930	2	1096	-1223	-16	950	885	15	626	514
-2	1234	-1774	-14	562	-576	4	1011	1172	-15	1189	-1239	16	585	675
0	1695	2109	-12	1100	1072	6	1099	-1207	-14	1092	-1150	17	597	-549
2	2715	-3437	-10	1097	-1245	8	981	1102	-13	1430	1502	18	571	-619
4	2092	2578	-8	1538	1885	10	791	-764	-12	1087	1122			
6	2635	-3906	-6	1476	-1931	12	555	559	-11	1561	-1716	4,1,L		
8	2505	3298	-4	1087	1431	14	261	-251	-10	1266	-1245			
10	1511	-1912	-2	1368	-1789				-9	1250	1308	-19	156*	-138
12	525	529	0	1966	2463	17,0,L			-8	680	757	-18	201*	143
14	373	-464	2	2086	-2475				-7	1176	-1335	-17	385	290
16	734	842	4	1989	2246	-13	382	432	-6	828	-884	-16	232*	-130
18	1025	-1060	6	1129	-1115	-11	617*	-392	-5	1250	1367	-15	429*	-330
			8	1241	1003	-5	503	450	-4	1316	1477	-14	364*	318
5,0,L			10	883	-976	-3	446	-538	-3	2721	-3708	-13	654	695
			12	1058	1139	-1	426	487	3	2448	2430	-12	174*	-437
-13	256	342	14	1157	-1232	1	117*	-128	4	1440	1457	-11	381*	-321
-9	719	724	16	1179	1135	5	172*	184	5	990	-1003	-10	875	783
-7	623	-786	18	771	-555	7	262*	119	6	914	-930	-9	262*	-152
-5	580	601							7	1365	1370	-8	896	-885
-3	290	-347	11,0,L			18,0,L			8	1627	1496	-7	510	-556
-1	1310	-1345							9	998	-1030	-6	750	808
1	539	716	-17	877	422	-12	526	628	10	1413	-1392	-5	560*	245
3	329*	228	-15	260	-306	-10	1407	-1016	11	1467	1409	-4	797	-932
5	893	-812	-13	430	562	-8	1131	1289	12	1062	1026	-3	384	-355
7	354	-300	-11	681	-688	-6	1094	-1341	13	1072	-1367	-2	834	838
9	298	384	-9	622	707	-4	866	868	14	679	-658	-1	1691	1686
11	86*	-171	-7	520	-440	-2	588	-573	15	1049	1082	0	500	-383
13	327*	218	-5	325*	-143	0	704	841	16	847	805	1	230*	-114
			-3	193*	-49	2	760	-790	17	500	-491			

* These reflections were treated as unobserveds.

TABLE 5.7 page 2

4,1,L

2	1164	-806
3	661	394
4	126*	207
5	48*	59
6	146*	0
7	88*	-90
9	475	446
10	205*	130
11	327	-358
12	280*	-259
13	253*	179
14	161*	-15
15	308*	-83
16	245*	245
17	341*	170
18	393	-402

5,1,L

-18	599	-524
-17	828	747
-16	594	527
-15	1124	-1029
-14	840	-789
-13	1095	1085
-12	783	712
-11	1276	-1132
-10	1295	-1294
-9	1197	1312
-8	1797	1993
-7	1708	-1856
-6	1628	-1834
-5	2061	2354
-4	1293	1605
-3	1724	-2083
-2	1222	-1356
-1	1512	1516
0	519	598
1	487	109
2	874	-746
3	2086	1758
4	1419	1189
5	3236	-2793
6	2126	-1796
7	2682	2419
8	1368	1219
9	2130	-2096
10	1305	-1142
11	1154	1070
12	917	829
13	712	-643
14	492	-439
15	833	642
16	561	570
17	670	-611
18	542	-562

6,1,L

-18	480	434
-17	115*	18
-16	501	-422
-15	290*	129
-14	371*	238
-13	502	435
-12	378	333
-11	702	-652
-10	368*	-238
-9	876	732
-8	256*	30
-7	327*	-224
-6	1082	1108
-5	737	-639
-4	715	-714
-3	651	535
-2	802	666
-1	326*	377
0	821	567
1	785	-525
2	1599	-1125
3	670	526
4	1429	1154
5	413*	-205
6	595	-417
7	421*	-257
8	258*	-159
9	969	883
10	170*	-166
11	430	-382
13	222*	65
14	372*	-316
16	292*	189
18	224*	-63

7,1,L

-17	451	384
-16	823	711
-15	687	-528
-14	707	-643
-13	1244	1118
-12	932	755
-11	1267	-1088
-10	1118	-1005
-9	2206	2065
-8	1600	1569
-7	1976	-1956
-6	2017	-2126
-5	1671	1843
-4	1008	1118
-3	1858	-2004
-2	894	-954
-1	1810	1736
0	875	910
1	1795	-1502
2	820	-781
3	2019	1653
4	2293	1828
5	2267	-1927
6	2311	-1984
7	1647	1374
8	1519	1337
9	1604	-1500
10	875	-746
11	1256	1179
12	405*	266
13	1081	-1148
14	519	-445
15	718	747
16	620	555
17	573	-608
18	468	-535

8,1,L

-18	377	380
-16	383	-364
-15	173*	68
-14	277*	140
-13	235*	158
-12	177*	-51
-11	1132	-957
-10	317*	-63
-9	1021	860
-8	253*	-28
-7	783	-616
-6	744	726
-5	294*	332
-4	1002	-1022
-3	742	661
-2	744	739
-1	224*	-89
0	248*	-151
1	824	-648
2	344*	-215
3	1238	871
4	733	554
5	905	-679
6	232*	-210
7	375*	-203
8	614	-323
9	317*	319
10	469	-365
11	447	-357
12	171*	194
13	379*	141
14	193*	-242
17	223*	170
18	166*	120

9,1,L

-18	569	-536
-17	344	311
-16	749	641
-15	320	-364
-14	671	-549
-13	994	871
-12	905	786
-11	1326	-1182
-10	528	-459
-9	1771	1722
-8	1280	1262
-7	1785	-1695
-6	1467	-1515
-5	1544	1542
-4	1258	1380
-3	1058	-1084
-2	1282	-1319
-1	1530	1432
0	1533	1444
1	1628	-1340
2	1195	-982
3	2222	1923
4	1184	1003
5	1787	-1425
6	1402	-1224
7	1033	867
8	1168	1074
9	960	-870
10	814	-711
11	1004	858
12	802	733
13	1262	-1298
14	788	-647
15	1045	1057
16	495	530
17	602	-542

10,1,L

-17	133*	178
-16	282*	-258
-14	254*	164
-13	205*	-59
-12	286*	-305
-11	448	-265
-10	1029	793
-9	152*	269
-8	415*	-12
-7	524	-358
-6	229*	111
-5	214*	172
-4	160*	-45
-3	135*	-191
-2	233*	-50
-1	253*	-94
0	1120	-902
1	203*	-71
2	952	748
3	333*	-250
4	357*	-328
5	228*	-3
6	46*	-99
7	185*	5
8	556	400
9	229*	-39
10	522	-528
12	231*	274
13	391*	90
17	96*	97

11,1,L

-17	635	630
-16	553	531
-15	801	-777
-14	699	-597
-13	981	837
-12	1065	953
-11	1091	-936
-10	1333	-1082
-9	712	675
-8	1054	964
-7	1019	-950
-6	1015	-1025
-5	1357	1315
-4	1191	1159
-3	1653	-1636
-2	871	-1180
-1	1643	1626
0	2030	1903
1	1924	-1690
2	1350	-1197
3	1592	1360
4	972	802
5	1174	-1041
6	737	-701
7	880	670
8	768	677
9	685	-683
10	1026	-938
11	728	672
12	968	945
13	996	-918
14	701	-673
15	847	906
16	404	460
17	579	-619

12,1,L

-15	199*	-145
-14	370	335
-13	185*	124
-12	553	-508
-10	876	698
-9	481*	307
-8	638	-522
-7	222*	-64
-6	235*	-56
-5	692	495
-4	279*	191
-3	971	-815
-2	255*	-290
-1	564	431
0	149*	-121
1	117*	149
2	897	714
3	490	-399
4	482*	-275
6	251*	212
7	224*	145
8	408*	340
9	492	-394
10	548	-432
12	146*	247
13	240*	-3
14	234*	-156
15	181*	-177
16	183*	74

13,1,L

-16	516	487
-15	950	-968
-14	678	-567
-13	1096	974
-12	1039	852
-11	793	-740
-10	1148	-994
-9	698	543
-8	677	566
-7	669	-609
-6	753	-647
-5	1277	1266
-4	658	637
-3	1865	-1747
-2	1013	-936
-1	1693	1568
0	1498	1506
1	1556	-1371
2	1613	-1456
3	1207	1003
4	922	792
5	1152	-974
6	616	-548
7	1270	1100
8	492	400
9	1146	-982
10	657	-623
11	1037	956
12	669	638
13	644	-606
14	582	-597
15	323	398

14,1,L

-15	342	-264
-14	448	413
-13	192*	182
-10	424	305
-8	248*	-210
-6	133*	-118
-5	126*	289
-4	276*	-180
-3	721	-616
-2	315*	139
-1	608	486
0	221*	-99
1	96*	69
4	305*	198
5	216*	213
7	390*	58
8	336*	-160
10	291*	54
12	164*	52
14	140*	-125

15,1,L

-9	884	667
-8	639	637
-7	876	-788
-6	717	-733
-5	835	739
-4	833	784
-3	1217	-1219
-2	1043	-1028
-1	1156	999
0	1185	1175
1	933	-816
2	1065	-970
3	1165	977
4	735	624
5	1152	-958
6	736	-644
7	1118	1171
8	562	574
9	912	-837
10	576	-575
11	666	655
12	487	508
13	387	-335
14	424	-476

16,1,L

-14	312	332
-13	105*	159
-12	346	-307
-10	308	276
-9	104*	0
-8	68*	-188
-7	227*	-180
-6	325*	194
-5	309*	226
-4	488	-445
-3	301*	-345
-2	347*	303
-1	214*	291
-1	281	281
0	368*	-177
3	314*	-6
4	530	441
5	115*	-105
6	61*	-77
7	101*	121
8	395	-393
9	148*	31
10	371	424
11	178*	-138
12	199*	-180
13	151*	72

17,1,L

-5	880	821
-4	771	702
-3	644	-585
-2	721	-712
-1	425	397
0	503	506
1	696	-654
2	605	-552
3	952	876
4	766	614
5	1033	-1053
6	831	-792
7	1220	946
8	778	767
9	668	-679
11	433	383
12	230*	302
13	272	-335

18,1,L

-12	111*	-69
-11	82*	-168
-9	145*	95
-5	52*	-22
-4	672	-648
-3	277*	-117
-2	232*	258
-1	123*	62
0	390*	-87
1	207*	79
2	406*	-66
4	322*	203
5	251*	-186
6	258*	-102
8	212*	-48
9	236*	66
10	280*	63

19,1,L

-3	631	-741
-2	517	-461
-1	461	400
0	535	564
1	500	-464
2	610	-517
3	701	712
4	651	698
5	753	-679
6	711	-727
7	748	783
8	589	664
10	377	-398

20,1,L

-8	29*	-266
-5	198*	-54
-4	139*	-132
-3	190*	31
-2	168*	39
-1	192*	94
0	155*	40
3	136*	199
4	220*	-109
5	217*	-254
8	201*	96

21,1,L

-5	320	430
-3	692	-620
-2	411	-416

* These reflections were treated as unobserveds.

TABLE 5.7 page 3

21,1,L

-1	559	598
0	310	317
2	369	-269
3	558	496
4	414	504
5	229*	-322
6	392	-515
7	230*	248

22,1,L

-5	190*	33
-2	161*	88
-1	125*	122
0	167*	-193
1	71*	-116
2	136*	242

0,2,L

2	468	600
3	2537	3017
4	970	-895
5	2794	-2901
6	580	518
7	2763	2847
8	270*	-293
9	1711	-1781
10	522	459
11	1492	1599
12	337*	-229
13	1073	-1269
14	173*	262
15	880	985
16	239*	-250
17	799	-869

1,2,L

-16	347	-433
-15	52*	-121
-14	273*	321
-13	537	-534
-11	849	778
-10	450	465
-9	850	-859
-8	677	-614
-6	278*	279
-5	1345	1235
-4	263*	-269
-3	1772	-1891
-2	312	-370
-1	803	812
2	1137	1028
3	2029	-1837
4	308	343
5	103*	69
6	270	-240
7	743	537
8	72*	-2
9	457	-471
10	561	-611
11	274*	234
12	145*	374
13	271*	-198
14	135*	-309
15	191*	313
16	203*	266
17	156*	-207
18	118*	-148

2,2,L

-19	311E	-631
-17	784	835
-16	368	-464
-15	1126	-1125
-14	469	512
-13	1349	1336
-12	151*	-138
-11	1348	-1353
-10	356*	55
-9	1273	1414
-8	229*	-220
-7	1417	-1551
-6	510	527
-5	2257	2337
-4	492	-581
-2	273*	-122
-1	1854	2550
1	2920	-3441
2	779	594
3	1422	1423
4	814	-701
5	2486	-2201
6	718	683
7	2339	2399
8	384	-318
9	2359	-2322
10	333	321
11	1711	1681
12	82*	4
13	991	-1100
14	193*	-93
15	826	821
17	707	-787
18	70*	114

3,2,L

-18	211*	305
-17	158*	315
-14	578	653
-13	319	-350
-12	234*	-100
-11	781	760
-10	259*	-74
-9	464	-477
-7	264*	211
-4	1223	-1376
-3	469	-533
-2	422	-306
-1	740E	-535
0	823E	395
1	1192E	739
2	140*	93
3	666	-513
4	241*	234
5	480	-364
6	121*	-72
7	422*	241
8	172*	-2
9	349	299
10	196*	-199
11	664	-593
12	340	338
13	206*	155
14	202*	-308
18	153*	-108

4,2,L

-18	98*	317
-17	801	829
-17	801	829
-15	1030	-1021
-14	228*	229
-13	1296	1286
-12	315*	-188
-11	1470	-1493
-10	222*	-7
-9	1709	1748
-8	509	-435
-7	1917	-2005
-5	2545	2707
-4	603	-636
-3	3095	-4090
-2	855	912
-1	3039	3483
0	177*	-101
1	3482	-3142
2	1162	-717
3	3390	2847
4	630	-506
5	1932	-1657
6	333*	180
7	1836	1733
8	573	-502
9	1858	-1868
10	606	527
11	1688	1674
12	189*	-139
13	1515	-1605
14	167*	-98
15	1206	1015
16	155*	99
18	203*	140

5,2,L

-18	152*	177
-16	218*	-366
-15	282*	280
-14	588	600
-12	387	-429
-11	359*	-261
-10	394	432
-8	272*	-235
-7	630	628
-6	168*	-40
-5	1096	-1037
-4	138*	-38
-3	717	841
-2	319*	241
-1	87*	-154
0	731	-583
1	371*	169
2	291*	234
3	2584	1845
4	241*	141
5	781	-590
6	713	-562
7	136*	252
8	231*	-125
9	510	439
10	198*	-83
11	714	-623
12	284*	103
13	214*	180
14	314	-303
15	303	388
18	69*	-283

6,2,L

-18	129*	53
-17	849	878
-16	186*	-205
-15	957	-978
-14	267*	321
-13	1138	1088
-12	592	-524
-11	1428	-1333
-10	790	723
-9	1981	1981
-8	681	-594
-7	2158	-2019
-6	522	515
-5	1845	1885
-4	399	-466
-3	2114	-2361
-2	453	438
-1	1561	1571
0	796	-729
1	2881	-2508
2	743	572
3	3061	2677
4	625	-550
5	2412	-2096
6	655	471
7	2085	1836
8	624	-500
9	1459	-1460
10	760	732
11	1121	1068
12	774	-770
13	1124	-1125
14	258*	25
15	749	940
16	130*	-56

7,2,L

-16	228*	-349
-15	51*	112
-14	148*	308
-13	141*	85
-12	504	-467
-11	803	-736
-10	670	629
-9	807	719
-8	604	-596
-7	105*	135
-6	451	385
-5	1283	-1166
-4	155*	-6
-3	1634	1455
-2	377*	-161
-1	454	-351
0	418	-253
1	541	-412
2	978	703
3	1514	1144
4	441*	-337
5	852	-652
6	186*	-183
7	380*	-207
8	451	415
9	606	545
10	259*	-211
11	201*	-224
12	53*	29
15	357*	261
16	176*	264
17	187*	-111

8,2,L

-16	197*	167
-15	1060	-1048
-13	1318	1206
-12	737	-633
-11	1025	-972
-10	715	633
-9	1406	1284
-8	414	-371
-7	1515	-1451
-6	284*	219
-5	1830	1895
-4	184*	10
-3	1864	-2077
-2	583	625
-1	2044	2106
0	1118	-1045
1	2342	-1963
2	1175	1014
3	2811	2528
4	685	480
5	2312	-1957
7	2025	1767
8	375	342
9	1390	-1331
10	92*	33
11	869	849
12	475	-588
13	1042	-1032
14	409	404
15	810	916
16	149*	-179

9,2,L

-17	157*	-338
-14	266*	309
-13	160*	-12
-12	299*	-250
-11	221*	-333
-10	353*	352
-9	453	385
-8	489	-531
-7	109*	4
-6	516	575
-5	333*	-280
-4	115*	-105
-3	184*	108
-2	460	-358
-1	170*	28
0	303*	259
1	554	439
2	325*	282
3	688	-600
4	331*	-275
5	220*	-5
8	121*	90
9	120*	-144
10	150*	-310
11	368	394
12	309*	250
13	406	-350
14	223*	-247
16	121*	76

10,2,L

-17	363	565
-16	130*	37
-15	949	-991
-14	83*	67
-13	1280	1217
-12	319	-420
-11	1398	-1377
-10	411	410
-9	1536	1380
-8	208*	-278
-7	1620	-1415
-6	459	460
-5	1801	1777
-4	224*	-180
-3	2017	-2025
-2	499	577
-1	2297	2358
0	1108	-977
1	2343	-2089
2	811	790
3	2425	2071
4	365*	-164
5	1800	-1541
6	185*	-91
7	1746	1473
8	293*	206
9	1615	-1522
10	136*	123
11	1174	1279
12	313	-330
13	863	-997

11,2,L

-16	254	-362
-14	404	420
-13	278*	-103
-12	168*	-174
-11	203*	140
-10	304	363
-9	539	-431
-8	92*	-151
-6	300*	320
-5	314*	213
-4	439	-397
-3	372	-417
-2	352*	241
-1	241*	232
0	145*	70
1	534	498
3	1320	-1107
4	169*	277
5	845	762
6	116*	104
7	311*	237
8	102*	86
9	654	-565
10	184*	9
11	605	496
12	133*	81
13	213*	-173
15	185*	-274
16	233*	118

12,2,L

-15	602	-630
-14	359	268
-13	1032	951
-12	364*	-300
-11	1444	-1359
-10	288*	179
-9	1555	1480
-7	1510	-1341
-6	467	314
-5	1316	1137
-4	742	-715
-3	1375	-1398
-2	518	588
-1	1515	1541
0	191*	-291
1	1823	-1586
2	460	463
3	1930	1854
4	358	-378
5	1470	-1291
6	299*	288
7	1205	1045
8	433	-295
9	1323	-1275
10	284*	217
11	982	1043
12	174*	11
13	712	-949
14	191*	69

13,2,L

-15	185*	104
-14	368	460
-13	289	-251
-12	456	-501
-11	520	427
-10	374	391
-9	436	-395
-8	280*	-273
-7	228*	102
-6	153*	168
-5	643	644
-4	247*	-241
-3	675	-756
-2	378	378
-1	364	382
0	408	-396
1	149*	139
2	523	464
3	1135	-990
4	44*	-101
5	557	469
6	43*	-24
8	242*	27
9	294*	-266
10	311*	42
11	219*	208
12	140*	-58
13	180*	-94
14	156*	-88

14,2,L

-14	252*	216
-13	686	729
-12	200*	-74
-11	820	-821
-10	172*	-14
-9	1346	1279
-8	95*	-249
-7	1321	-1294
-6	223*	225
-5	1424	1358
-4	503	-635
-3	1380	-1425
-2	320*	268
-1	1203	1173
0	62*	-254
1	1431	-1437
2	365	375
3	1652	1584

* These reflections were treated as unobserveds

TABLE 5.7 page 4

14,2,L

4	534	-515
5	1316	-1223
6	369	446
7	1133	1048
8	504	-458
9	864	-785
10	213*	138
12	187*	121
14	79*	-180

15,2,L

-13	208*	-150
-12	288*	-279
-11	213*	171
-10	283	312
-8	402	-425
-7	215*	88
-6	353	295
-5	138*	191
-4	177*	-292
-3	293*	-289
-2	211*	51
-1	366*	142
0	207*	-196
2	207*	235
3	235*	69
4	160*	12
5	243*	44
6	175*	33
7	108*	50
8	203*	101
9	224*	161
10	198*	-238

16,2,L

-11	632	-603
-10	291*	212
-9	836	847
-8	511	-441
-7	1133	-1125
-6	589	588
-5	1237	1215
-4	304*	-283
-3	1402	-1405
-2	131*	-70
-1	1185	1106
0	226*	76
1	932	-916
3	910	903
4	579	-703
5	1030	-999
6	524	471
7	1017	980
8	396	-356
9	930	-920
10	108*	114
12	177*	3

17,2,L

-9	171*	-27
-8	65*	-231
-7	238*	260
-6	374	422
-5	530	-431
-3	299	250
-2	229*	-27
-1	257*	-204
0	42*	4
1	116*	-136
2	313*	-9
3	406	369
4	308*	-172
5	231*	-207
6	261*	171
7	88*	-74
8	148*	-58
9	311*	346
10	198*	-48
11	232*	-453
12	63*	174

18,2,L

-9	673	725
-7	914	-801
-6	292	412
-4	283*	-89
-3	1000	-1091
-2	83*	-42
-1	1009	981
0	271*	-39
1	1022	-1009
2	278*	288
3	1028	1036
4	275*	-425
5	848	-833
6	341	364
7	800	784
8	57*	-147

19,2,L

-9	187*	205
-8	203*	-179
-7	103*	186
-6	177*	221
-5	445	-327
-4	273*	-306
-3	253*	252
-2	175*	145
-1	92*	74
0	88*	-148
1	354	-365
2	222*	56
3	277*	262
4	151*	-122
5	238*	-255
6	118*	110
8	75*	-198
9	116*	96

20,2,L

-6	135*	131
-4	86*	-128
-3	780	-805
-2	303	281
-1	831	836
0	326	-339
1	811	-871
2	285*	346
3	790	895
4	118*	-89
5	670	-707
6	139*	-49
8	74*	62

21,2,L

-5	178*	-113
-4	224*	-173
-3	110*	108
-2	212*	146
-1	193*	-70
0	239*	-236
1	233*	24
2	205*	235
3	175*	46

22,2,L

2	89*	176

0,3,L

1	613	683
2	508	-531
3	1585	-1468
4	559	465
5	156*	43
6	549	-493
7	821	789
8	146*	-31
9	835	-785
10	217*	177
11	736	731
13	156*	-120
14	242*	-221
15	215*	-226
18	155*	-63

1,3,L

-15	164*	-36
-14	1023	1014
-13	51*	227
-12	784	-831
-11	772	-788
-10	1260	1287
-9	1227	1306
-8	1680	-1891
-7	1333	-1451
-6	2703	3170
-5	1039	1114
-4	2611	-2942
-3	933	-1006
-2	1147	1600
0	1222	-1243
1	399	-368
2	1304	1205
3	808	842
4	1721	-1887
5	988	-994
6	2488	2671
7	954	811
8	2091	-2197
9	1043	-1000
10	1528	1543
11	1035	928
12	1169	-1231
14	934	893

2,3,L

-17	175*	-287
-15	70*	145
-14	340*	161
-13	136*	-176
-12	340	338
-11	303	335
-10	296	-290
-8	310	-286
-7	274	389
-6	890	964
-5	86*	-63
-4	664	-725
-3	331	-296
-2	173*	403
-1	176*	-47
0	335*	212
1	837	-565
2	258*	170
3	362	-321
4	54*	73
5	182*	-87
6	185*	61
7	256	338
8	155*	51
9	797	-713
10	210*	-315
11	676	585
14	162*	-222
15	156*	-28
16	109*	-4
17	93*	77

3,3,L

-17	120*	78
-15	333	-272
-12	1405	-1295
-11	943	-870
-10	1691	1494
-9	1415	1446
-8	1035	-1168
-7	1055	-1233
-6	1909	2084
-5	1229	1399
-4	2139	-2715
-3	973	-1200
-2	2018	2541
-1	557	724
0	2770	-2557
1	1410	-1114
2	2632	2297
3	1079	969
4	2184	-2070
5	1251	-1079
6	1910	1933
7	567	531
8	1679	-1853
9	748	-648
10	2044	1898
11	965	959
12	1631	-1616
14	1163	1216

4,3,L

-16	64*	-177
-15	145*	425
-14	246*	76
-13	306	-285
-12	190*	94
-11	260	359
-10	64*	130
-9	193*	118
-8	640	-568
-7	229*	416
-6	365	312
-5	126*	-62
-4	61*	9
-3	928	982
-2	631	-622
-1	812	-692
0	719	590
1	762	-603
2	992	888
3	921	727
4	400	-232
5	334	-352
6	292	281
7	331*	295
8	362	312
16	137*	-18
18	163*	154

5,3,L

-15	390	-508
-14	985	881
-13	840	676
-12	1477	-1376
-11	500	-493
-10	1663	1583
-8	1797	-1668
-7	286	-367
-6	1560	1758
-5	340	437
-4	1610	-1980
-3	1015	-1205
-2	1921	1985
-1	1713	1737
0	3143	-3019
1	1903	-1707
2	2751	2528
3	1808	1498
4	2441	-2225
5	372	-286
6	1029	1017
7	447	304
8	1085	-1101
10	1421	1306
12	1727	-1651
14	1185	1232

6,3,L

-18	66*	72
-14	119*	73
-13	697	-594
-11	269	245
-10	77*	214
-8	198*	-125
-6	369	447
-5	89*	56
-4	540	437
-3	615	624
-2	868	-799
-1	656	-598
0	105*	11
1	135*	-14
2	493	393
3	987	752
4	1325	-1046
5	443	-375
6	103*	12
7	396	364
8	102*	286
9	269	257
10	179*	-254
14	89*	-73

7,3,L

-16	938	-855
-14	1065	1020
-13	989	817
-12	1257	-1138
-10	1264	1190
-8	1151	-1107
-7	584	-528
-6	1256	1266
-5	768	826
-4	988	-1192
-3	1530	-1648
-2	2026	1979
-1	1441	1320
0	2054	-1878
1	1266	-1085
2	2111	1915
3	1605	1333
4	2257	-2018
5	516	-442
6	1705	1498
7	671	567
8	831	-792
9	538	-437
10	858	901
12	1095	-1119
17	136*	-338

8,3,L

-14	361	350
-13	295	-343
-12	503	-432
-11	172*	95
-9	304	-348
-8	360	-383
-7	665	724
-6	102*	62
-5	602	-805
-4	70*	-48
-3	343	353
-2	258*	186
-1	338	-307
0	663	-583
1	567	-437
2	376	283
3	673	528
4	283*	87
5	278	-198
6	149*	23
7	94*	16
8	280*	22
9	171*	-39
10	289*	247
11	36*	108
12	211*	-317
14	191*	-128
15	116*	180
16	185*	180

9,3,L

-16	809	-806
-15	721	-649
-14	1288	1144
-13	735	616
-12	1532	-1454
-11	832	-712
-10	1336	1171
-9	726	657
-8	1076	-1046
-7	669	-680
-6	1195	1166
-5	707	747
-4	1528	-1622
-3	497	-590
-2	2066	1980
-1	808	721
0	2201	-1777
1	595	-744
2	1992	1809
3	987	859
4	1894	-1659
5	1492	-1363
6	2094	1921
7	1012	900
8	1623	-1499
9	924	-858
10	1401	1545
11	500	532
12	865	-1004
17	160*	-175

10,3,L

-14	223*	376
-13	242*	-377
-12	342	-251
-10	178*	108
-9	62*	-181
-8	123*	-29
-7	301	354
-6	275*	174
-5	521	-588
-4	484	-469
-3	327	248
-1	198*	181
0	187*	-139
1	459	-393
2	249	-227
3	389	379
4	548	495
5	202*	99
6	327	-288
10	508	467
11	262	247
13	226*	-310
14	169*	-88
15	115*	110

11,3,L

-15	261	-328
-14	961	878
-13	505	445
-12	1314	-1229
-11	636	-525
-10	1382	1194
-8	1115	-1017
-7	1183	-1144
-6	1324	1293
-5	808	765
-4	1264	-1285
-3	452	-496
-2	1271	1304
-1	329	208
0	1494	-1432
1	384	-396
2	1321	1188
3	1164	1011
4	1495	-1239
5	1406	-1212
6	1554	1462
7	1056	968
8	1320	-1190

* These reflections were treated as unobserveds.

TABLE 5.7 page 5

	11,3,L	
9	650	-622
10	1130	1198
11	375	364
	12,3,L	
-14	83*	159
-12	35*	53
-11	528	495
-10	193*	-66
-9	329*	-340
-8	216*	38
-6	488	418
-5	121*	-76
-4	590	-569
-3	212*	-136
-2	454	377
-1	348	-372
0	272*	-270
1	273	231
2	213*	-47
4	566	417
5	152*	-60
6	275	-260
7	252	290
8	254	-216
9	56*	-250
10	245*	185
12	69*	-107
13	34*	-66
14	215*	2
	13,3,L	
-13	54*	147
-12	767	-810
-10	1169	1063
-9	812	775
-8	1478	-1429
-7	1010	-980
-6	1574	1553
-5	847	750
-4	1339	-1311
-3	459	-463
-2	1002	925
-1	334	308
0	890	-787
1	351	-331
2	939	825
3	336	319
4	1422	-1317
5	707	-592
6	1689	1644
7	659	587
8	1147	-1057
9	610	-593
10	876	934
11	471	517
12	663	-752
13	319E	-421
	14,3,L	
-12	138*	117
-11	656	630
-10	188*	5
-9	586	-572
-8	292	-156
-7	581	594
-6	369	385
-4	567	-487
-3	105*	70
-2	180*	71
-1	405	-415
0	128*	56
1	657	644
2	345*	219
3	535	-456
4	160*	-20
6	230*	84
7	349	405
8	114*	39
9	355	-388
10	142*	-137
11	171*	168
12	144*	59
13	47*	124
	15,3,L	
-12	528	-491
-10	478	613
-9	724	644
-8	1068	-1023
-7	497	-430
-6	1407	1430
-5	770	709
-4	1448	-1356
-3	622	-633
-2	834	735
-1	570	598
0	771	-765
1	817	-805
2	677	482
3	529	538
4	1076	-1079
5	428	-328
6	1158	1147
7	388	315
8	878	-898
9	411	-453
10	612	656
11	485	627
	16,3,L	
-12	139*	-169
-11	303	350
-10	176*	141
-8	315	-243
-7	326*	350
-6	70*	7
-5	203*	-152
-3	234*	-24
-2	227*	-6
-1	245*	140
0	154*	-24
1	115*	63
2	337	442
3	134*	-110
4	405	-402
5	195*	-52
6	218*	95
7	55*	186
8	64*	62
9	68*	-132
10	227	-283
	17,3,L	
-10	635	605
-9	68*	181
-8	563	-523
-7	139*	-69
-6	956	976
-5	379	412
-4	975	-955
-3	792	-739
-2	1038	994
-1	850	910
0	1008	-993
1	773	-755
2	879	766
3	373	464
4	736	-703
5	73*	42
6	743	737
7	194*	28
8	636	-699
9	244*	-178
	18,3,L	
-9	103*	-133
-8	117*	-107
-7	99*	262
-6	87*	5
-5	441	-365
-4	260	261
-3	358	336
-2	176*	-112
-1	289	-207
0	209*	-185
1	173*	-35
2	375	332
3	300*	-38
4	350	-376
5	237*	-166
6	240*	2
7	181*	-104
8	71*	162
9	183*	194
	19,3,L	
-9	74*	41
-7	41*	-170
-6	478	527
-5	291	286
-4	618	-615
-3	567	-570
-2	832	806
-1	597	567
0	1001	-1047
1	397	-356
2	958	1008
3	380	412
4	605	-570
5	245	-209
6	348	401
7	176*	199
9	318	-259
	20,3,L	
-5	246	-245
-4	109*	-19
-3	414	419
-2	141*	1
-1	212	-281
0	235*	-46
1	197*	-19
2	104*	154
3	92*	62
4	98*	-71
5	149*	-43
	21,3,L	
-5	319	329
-3	274	-271
-2	504	579
-1	194	184
0	669	-683
1	266	-289
2	720	767
	22,3,L	
-3	172	180
-2	125*	34
-1	121	-182
	0,4,L	
2	1066	1388
3	858	-800
4	1854	-2340
5	728	706
6	2492	2633
7	945	-902
8	1633	-2035
9	485	361
10	1651	1647
11	277*	-352
12	909	-918
13	456	397
14	606	616
15	618	-579
16	685	-713
17	332	356
18	698	699
	1,4,L	
-18	352*	-337
-17	71*	-188
-16	124*	136
-15	250*	189
-14	270*	151
-13	206*	-171
-12	143*	-89
-11	297*	258
-10	231*	-237
-9	462	-439
-8	377*	359
-7	220*	219
-6	268*	-93
-5	418	-545
-3	244*	141
-2	298*	470
-1	294*	-541
0	149*	88
1	248*	-187
2	458	-427
3	295*	255
4	164*	17
5	192*	-76
6	194*	174
7	315*	334
8	829	-726
9	276*	-299
10	394	406
11	48*	127
12	292*	-262
13	327*	-325
15	287*	248
16	255*	94
17	245*	-213
18	265*	175
	2,4,L	
-17	245*	-354
-16	622	-625
-15	350*	270
-14	441	366
-13	522	-495
-12	863	-891
-11	554	494
-10	1658	1689
-9	656	-600
-8	1916	-2399
-7	893	976
-6	2061	2865
-5	524	-552
-4	1568	-2223
-3	834	1163
-2	956	1357
-1	955	-1202
0	1573	-1403
1	781	640
2	2182	1735
3	754	-685
4	2327	-2242
5	377	311
6	2332	2158
7	835	-798
8	1587	-1333
9	1174	1091
10	1230	1222
11	716	-697
12	1215	-1249
13	610	590
14	1142	1213
15	372	-470
16	999	-1008
17	303	304
	3,4,L	
-18	143*	-220
-17	100*	-336
-16	362	426
-15	169*	155
-14	140*	-154
-13	185*	-307
-12	193*	9
-11	166*	299
-10	34*	102
-9	479	-513
-8	185*	-20
-7	686	653
-6	206*	188
-5	107*	-89
-4	579	627
-3	164*	-15
-2	435	-452
-1	135*	-203
0	530	491
1	866	668
2	119*	8
3	823	-604
4	209*	146
6	330*	313
7	35*	132
8	226*	-229
9	302	-417
10	200*	164
11	579	605
12	139*	-34
13	366	-389
14	114*	-30
15	310	281
18	76*	-26
	4,4,L	
-18	678	672
-16	903	-850
-15	387	313
-14	1061	911
-13	411	-459
-12	1033	-1014
-11	564	662
-10	1389	1292
-9	1133	-1032
-8	1796	-1648
-7	858	845
-6	1345	1741
-5	424	-578
-4	1598	-2094
-3	694	789
-2	1620	1723
-1	1055	-1151
0	2916	-2721
1	1888	1542
2	2554	2107
3	1963	-1538
4	1863	-1604
5	562	401
6	1559	1547
7	475	-411
8	789	-654
9	697	580
10	1062	989
11	716	-605
12	1381	-1459
13	499	400
14	1181	1256
15	443	-472
16	1004	-1058
	5,4,L	
-18	112*	-92
-17	401	-394
-16	270*	210
-15	274*	223
-14	482	-443
-13	403*	-310
-12	351	284
-11	289*	240
-10	450	-346
-9	192*	-144
-8	414	-354
-7	482	391
-6	480	558
-5	164*	55
-4	178*	-103
-2	152*	-30
-1	148*	-30
0	235*	172
1	258*	-96
2	250*	38
3	163*	22
4	371*	-236
5	378*	183
6	225*	-50
7	99*	232
8	233*	87
9	458*	-242
10	287*	310
11	821	728
12	236*	-119
13	355	-461
14	366	483
15	221*	282
18	69*	169
	6,4,L	
-17	240*	-351
-16	942	-915
-15	363	256
-14	1339	1310
-13	187*	-105
-12	1550	-1542
-11	395	487
-10	1066	918
-9	957	-972
-8	598	-558
-7	1007	858
-6	787	824
-5	484	-482
-4	1699	-1827
-3	579	546
-2	2924	3050
-1	834	-823
0	3606	-3115
1	1554	1341
2	2807	2375
3	1097	-873
4	1679	-1361
5	1257	1028
6	855	733
7	499	-419
8	1041	-895
9	463	335
10	1339	1080
11	238*	-110
12	1465	-1448
13	284*	283
14	1056	1128
15	408	-429
16	620	-730
17	321	388
	7,4,L	
-15	444	439
-14	112*	-232
-13	510	-548
-12	172*	109
-11	467	432
-10	395*	-252
-8	142*	140
-7	227*	161
-6	407*	-298
-5	253*	-255
-4	158*	-4
-3	434	473
-2	200*	-19
-1	533	-399
0	266*	182
1	146*	-94
2	585	-476
3	106*	32
4	132*	106
5	192*	101
6	513	-436
7	266*	-112

* These reflections were treated as unobserveds.

TABLE 5.7 page 6

	7,4,L	
8	277*	126
9	631	581
10	222*	178
11	130*	-49
12	270*	-155
13	256*	-287
14	210*	177
15	242*	301
17	239*	-341
	8,4,L	
-17	314	-332
-16	962	-923
-15	443	368
-14	1383	1325
-13	417*	-271
-12	1604	-1471
-11	245*	303
-10	1322	1226
-9	816	-770
-8	781	-704
-7	798	723
-6	1148	1160
-5	840	-811
-4	1312	-1445
-3	512	402
-2	2159	2184
-1	693	-688
0	2960	-2673
1	792	658
2	2443	2117
3	608	-472
4	1314	-1317
5	825	639
6	1176	1083
7	850	-667
8	1273	-1083
9	792	677
10	1420	1249
11	311*	-240
12	1008	-1020
13	425	284
14	697	711
15	251*	-141
16	380	-439
	9,4,L	
-16	177*	146
-15	458	459
-13	774	-699
-12	279*	60
-11	641	530
-10	377	-277
-9	162*	-196
-8	400*	289
-7	161*	-84
-6	509	-425
-5	296*	-269
-4	358*	227
-3	651	634
-2	267*	150
-2	304*	150
-1	622	-558
0	879	-744
1	145*	158
2	635	530
3	135*	224
4	311*	201
5	318*	-234
6	401*	-315
7	232*	-142
8	368*	319
9	182*	302
10	263*	205
11	501*	-274
12	318*	-274
13	350*	-144
14	200*	197
15	248*	240
16	214*	-163
	10,4,L	
-16	734	-764
-15	456	472
-14	1001	918
-13	757	-620
-12	1158	-1104
-11	715	601
-10	1490	1344
-9	533	-537
-8	1545	-1289
-7	468	438
-6	1599	1572
-5	586	-563
-4	1482	-1458
-3	856	853
-1	1051	-1039
0	1358	-1220
1	992	939
2	1699	1419
3	911	-823
4	1804	-1703
5	581	532
6	2095	1944
7	1126	-971
8	1589	-1457
9	872	802
10	825	903
11	442	-384
12	590	-539
13	214*	212
14	354	400
	11,4,L	
-16	116*	81
-14	235*	-5
-13	187*	-236
-12	245*	12
-11	331*	226
-9	313*	-232
-7	535	484
-6	152*	-104
-5	398	-281
-4	315*	111
-3	374*	269
-2	234*	-160
-1	418*	-392
0	513	-454
1	219*	-72
2	218*	93
3	150*	-84
4	178*	-129
6	225*	69
7	368*	184
8	126*	117
9	67*	19
11	179*	-54
12	194*	25
14	239*	92
15	113*	23
	12,4,L	
-15	298*	312
-14	478	445
-13	430*	-266
-12	702	-656
-11	464*	222
-10	1210	1055
-9	651	-566
-8	1557	-1424
-7	575	507
-6	1930	1764
-5	610	-571
-4	1486	-1489
-3	737	696
-2	800	738
-1	765	-697
0	554	-549
1	707	629
2	1010	921
3	472	-413
4	1561	-1425
5	140*	133
6	1758	1725
7	330*	-325
8	1464	-1416
9	545	540
10	725	814
11	425	-381
12	465	-393
13	338	255
14	325	347
	13,4,L	
-14	265*	-88
-13	77*	-18
-12	96*	156
-11	72*	128
-10	73*	-74
-9	440	-394
-8	99*	95
-7	558	523
-6	95*	113
-5	445	-399
-4	430	264
-3	227*	204
-2	439	-313
-1	96*	25
0	509	502
1	233*	-43
2	186*	-211
3	316*	-273
4	209*	-34
5	514	395
6	121*	90
7	233*	5
8	348	-320
9	157*	-173
10	248*	42
11	167*	166
12	285*	232
13	71*	-176
14	255*	-220
	14,4,L	
-13	256*	-165
-12	714	-656
-11	313*	188
-10	1040	997
-9	548	-436
-8	1434	-1219
-7	679	682
-6	1569	1491
-5	688	-619
-4	1402	-1395
-3	640	685
-2	1048	961
-1	492	-527
0	933	-954
1	307*	176
2	933	837
3	571	-581
4	1223	-1232
5	534	403
6	1309	1198
7	503	-529
8	1048	-1054
9	451	439
10	731	815
11	300*	-311
12	557	-620
	15,4,L	
-13	120*	-157
-11	412*	163
-10	178*	-126
-9	292*	-295
-8	236*	24
-7	392	356
-6	81*	-46
-4	212*	-56
-3	202*	14
-2	120*	17
-1	58*	-119
0	200*	257
1	309*	264
2	262*	-24
3	547	-466
4	141*	-25
5	231*	352
6	281*	178
7	57*	56
8	227*	-314
9	259*	-158
10	143*	151
11	161*	257
13	69*	-155
	16,4,L	
-11	201*	173
-10	864	824
-9	259*	-238
-8	1095	-928
-7	530	550
-6	984	829
-5	389	-359
-4	1165	-1135
-3	666	619
-2	1243	1156
-1	537	-484
0	1252	-1250
1	490	588
2	1224	1200
3	403	-387
4	921	-919
5	315	371
6	540	599
7	337	-411
8	519	-449
9	282*	331
10	567	597
11	268*	-243
	17,4,L	
-10	169*	7
-9	189*	-316
-8	156*	-124
-7	254*	195
-6	102*	107
-5	214*	148
-4	56*	27
-3	232*	-20
-2	56*	40
-1	344	-370
0	157*	32
1	347*	327
2	316*	-172
3	256*	-316
4	269*	58
5	274*	188
6	140*	-147
7	111*	81
8	135*	-81
9	105*	-82
10	153*	147
	18,4,L	
-9	229*	-304
-7	270*	261
-6	561	523
-5	332*	-196
-4	758	-776
-3	85*	256
-2	1047	1161
-1	508	-518
0	1028	-1080
1	606	677
2	850	931
3	390	-361
4	632	-707
5	282	264
6	329	359
7	134*	-99
8	340	-282
9	238*	169
	19,4,L	
-7	230*	111
-3	305*	-40
-2	247*	55
-1	228*	-262
0	181*	3
1	223*	145
3	183*	0
4	210*	56
5	32*	54
7	88*	-26
	20,4,L	
-5	265*	-111
-3	208*	135
-2	887	899
-1	342	-327
0	944	-877
1	333	517
2	712	659
3	392	-484
4	551	-603
5	235	275
	21,4,L	
-4	145*	-19
-3	186*	243
-2	203*	43
-1	184	-163
0	170*	-95
1	70*	-10
2	95*	0
4	127*	123
	0,5,L	
3	623	-665
4	990	-1126
7	79*	-93
8	171*	-121
	1,5,L	
-12	190*	-128
-11	1448	1401
-10	372	400
-9	1959	-2068
-8	859	-731
-6	874	884
-5	1517	-1848
-4	329	-296
-3	1525	1693
-2	504	367
0	261*	-217
2	978	873
6	1365	1413
7	1705	-1737
9	1705	1613
10	200*	240
11	1034	-1044
12	125*	47
13	1049	1055
14	163*	-7
	2,5,L	
-17	251*	117
-11	312*	186
-10	490*	-316
-9	550	-487
-8	157*	133
-7	361*	252
-6	104*	-138
-5	370	427
-4	534	553
-3	283	-299
-2	436	-414
-1	526	619
0	736	635
1	224	298
2	178*	38
3	180*	-86
4	487	-439
6	437	389
11	76*	-18
14	165*	171
	3,5,L	
-16	298	-248
-14	134*	82
-12	281*	-171
-11	1108	1004
-10	408	338
-9	1780	-1893
-8	659	-585
-7	1855	2105
-6	419	386
-5	1519	-1736
-4	172*	-172
-3	1359	1487
-2	499	334
-1	2209	-1812
0	687	-612
2	798	672
3	2297	-2422
4	785	-699
7	1327	-1502
8	84*	-420
13	1126	1171
15	1246	-1296
	4,5,L	
-17	195*	-3
-16	243*	329
-15	245*	-123
-13	191*	67
-12	260*	282
-11	125*	68
-10	430	-364
-9	231*	-168
-8	294	296
-7	232*	232
-6	220*	64
-5	297*	-175
-4	277*	-153
-3	185*	-5
-2	192*	-11
-1	502	445
0	689	515
1	441	-405
2	822	-709
3	129*	-92
4	287*	155
6	185*	214
7	133*	33
11	189*	-76
12	94*	-372
14	56*	181
16	99*	-23
	5,5,L	
-15	1017	947
-13	1239	-1108
-12	558	-490
-11	1112	1090
-10	534	370
-9	1460	-1471
-8	487	-297
-7	1502	1412
-6	140*	38
-5	1366	-1418
-4	533	-565
-3	1896	2115
-2	473	509
-1	2591	-2216
0	960	-873
1	2670	2044
2	1168	1041
3	1826	-1741

* These reflections were treated as unobserveds.

TABLE 5.7 page 7

	5,5,L	
4	382	-220
5	1384	1279
7	1414	-1374
10	171*	509
	6,5,L	
-15	179*	152
-14	454	-391
-13	246*	25
-11	162*	-34
-10	659	-611
-8	83*	92
-7	317*	219
-6	79*	-30
-5	470	-421
-4	313*	-221
-3	630	592
-1	438	-389
0	105*	-143
1	323	-236
2	121*	-41
3	480	328
4	144*	45
5	489	-446
9	206*	339
13	247*	80
	7,5,L	
-16	157*	-197
-15	1082	993
-14	444	346
-13	1466	-1283
-12	595	-508
-11	1422	1233
-10	729	553
-9	1040	-978
-8	234*	-207
-7	812	853
-5	1046	-1006
-4	374	-332
-3	1794	1810
-2	753	685
0	1380	-1249
2	684	499
3	1590	-1524
4	275*	-273
5	1200	1119
7	1225	-1085
9	1602	1701
10	913	806
11	1344	-1245
12	399	-573
16	142*	-81
	8,5,L	
-16	191*	185
-15	380	322
-14	517	-557
-12	765	740
-11	210*	-240
-10	881	-825
-9	602	520
-8	179*	112
-7	386	-287
-6	239*	73
-5	273*	-161
-4	171*	111
-3	239*	212
-2	187*	45
-1	702	-630
0	222*	138
1	263*	-257
2	220*	4
3	518	371
4	249*	-151
5	145*	-176
10	103*	-50
12	112*	-65
13	164*	100
16	149*	-322
	9,5,L	
-15	937	919
-14	273	218
-13	1116	-1026
-11	1113	1096
-10	261*	203
-9	1376	-1340
-7	1392	1368
-6	278*	250
-5	1484	-1348
-4	384	-406
-3	1467	1562
-2	749	721
-1	1882	-1872
0	495	-483
1	1746	1754
2	493	350
3	1471	-1422
4	437	-330
5	1459	1390
7	1495	-1471
9	1398	1464
11	1055	-1094
13	579	788
	10,5,L	
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-13	284	-229
-12	407	417
-10	517	-484
-8	574	417
-7	257*	64
-6	325	-363
-5	65*	-46
-4	411	421
-3	83*	7
-2	318	-320
-1	474	-432
0	194*	119
1	151*	114
2	209*	50
3	279*	-263
4	298	-315
5	143*	44
6	295	226
9	219*	-232
10	213*	140
11	177*	12
13	145*	36
	11,5,L	
-15	730	701
-14	166*	61
-13	758	-731
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-11	839	728
-9	1306	-1249
-7	1531	1456
-6	599	518
-5	1370	-1289
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-1	774	-711
0	385	-322
1	894	791
2	72*	58
3	1268	-1076
4	443	-356
5	1384	1338
7	1491	-1526
9	1064	1128
11	574	-739
12	135*	-82
14	244*	84
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-14	134*	57
-13	115*	-180
-12	152*	-76
-11	205*	224
-9	233*	-118
-8	589	597
-6	824	-706
-5	155*	-96
-4	653	693
-3	453	-273
-1	427	392
0	440	-371
1	396	296
2	441	450
3	432	-373
4	384*	-316
5	485	398
6	172*	84
7	247*	-171
10	115*	198
11	151*	288
13	150*	-121
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-12	146*	-149
-11	924	806
-9	1114	-1041
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-7	1263	1232
-6	519	436
-5	1284	-1212
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-3	1142	1031
-2	263*	110
-1	1058	-1049
0	261	-252
1	1087	934
2	436	339
3	1220	-1171
4	681	-579
5	1240	1172
7	1221	-1241
9	1004	1058
10	114*	20
12	98*	-59
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-12	134*	-75
-11	319	260
-9	411	-360
-8	244*	296
-7	192*	182
-6	584	-497
-4	694	698
-3	187*	-242
-2	304*	-95
-1	410	431
0	286*	43
1	134*	123
2	178*	9
3	103*	-184
6	109*	-154
9	154*	-52
11	136*	225
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-12	158*	-152
-11	882	873
-10	240*	254
-9	1042	-1015
-8	290*	-267
-7	1027	1037
-6	285	249
-5	917	-831
-3	972	949
-2	200*	-64
-1	1170	-1113
0	250*	-155
1	1232	1235
2	397	406
4	203*	-250
	16,5,L	
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-10	226*	-244
-9	382	-353
-8	206*	121
-7	209*	277
-5	96*	-135
-3	62*	64
-2	334	-322
-1	146*	82
0	311	274
3	79*	-161
4	104*	28
5	164*	79
7	39*	62
8	98*	-210
	17,5,L	
-10	172*	148
-8	315	-290
-7	825	783
-6	268*	225
-5	707	-614
-4	257*	-222
-3	856	805
-2	104*	81
-1	890	-840
0	254*	-150
6	152*	202
8	181*	-212
	18,5,L	
-8	202*	246
-5	94*	-181
-3	262	252
-2	173*	-157
-1	120*	-171
1	48*	29
4	177*	120
5	98*	-71
6	200*	1
7	152*	72
	19,5,L	
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0	275*	-249
6	96*	38
	20,5,L	
-3	128*	314
-2	46*	-91
-1	238	-301
3	175*	125
4	130*	5
	21,5,L	
-1	449	-573
	0,6,L	
3	1316	-1516
4	1044	1150
5	1369	1533
6	890	-903
7	1022	-1076
8	1108	1069
9	919	944
10	886	-818
11	562	-512
12	1007	1020
13	792	798
14	600	-587
15	799	-835
16	172*	226
	1,6,L	
-16	198*	280
-15	201*	-325
-13	185*	99
-11	280*	238
-9	625	-626
-8	290*	109
-7	51*	-2
-6	182*	32
-5	675	665
-4	104*	-73
-3	834	-857
-2	373	302
0	281*	94
1	363	406
2	128*	92
3	689	-790
4	104*	-105
5	738	682
7	266*	-68
8	219*	-193
9	755	-693
10	563	664
11	334*	210
12	115*	-264
14	155*	259
16	307*	-315
	2,6,L	
-16	247*	197
-15	855	876
-14	332	-288
-13	950	-910
-12	759	648
-11	989	958
-10	1023	-983
-9	1245	-1257
-8	928	888
-7	996	1051
-6	991	-1139
-5	999	-1249
-3	1045	1084
-2	872	1084
-2	749	-701
0	1616	1336
2	1444	-1137
4	1384	1180
5	1842	1810
6	865	-845
7	1262	-1214
8	545	484
9	764	677
10	554	-538
11	725	-600
12	698	639
13	627	745
14	668	-688
15	733	-777
	3,6,L	
-16	104*	77
-15	134*	-286
-14	107*	-46
-13	128*	56
-12	266*	193
-11	201*	32
-10	320*	-509
-9	163*	51
-8	259*	341
-7	208*	101
-6	196*	-269
-5	175*	141
-3	74*	-89
-2	98*	-115
-1	91*	108
0	74*	56
1	272*	-212
2	494	405
3	440	338
4	214*	-187
5	248*	-82
6	141*	-62
7	282*	-207
9	350	412
10	106*	152
11	86*	-202
13	128*	392
15	186*	-6
16	151*	-150
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-16	403*	386
-15	608*	610
-14	378	-297
-13	1100	-1017
-12	551	500
-11	1356	1305
-10	662	-595
-9	1322	-1343
-8	584	601
-7	1098	1112
-6	1141	-1288
-5	777	-738
-4	1181	1435
-3	691	807
-2	994	-1170
-1	993	-1047
0	1071	1129
2	1141	-1007
3	1774	-1656
4	1192	977
5	1595	1391
6	1071	-954
7	1389	-1320
8	726	632
9	819	815
11	776	-697
12	454	517
13	698	741
14	666	-647
15	551	-580
	5,6,L	
-16	150*	123
-15	166*	-139
-14	386*	-171
-13	160*	136
-12	328*	466
-11	327*	-266
-10	563	-449
-9	402	391
-8	417	366
-7	352*	-238
-6	125	-46
-5	417	-431
-4	263	347
-3	650	679
-2	260*	-315
-1	577	-520
0	152*	-14
1	164*	-120
2	291*	-158
3	948	783
4	206*	-83
5	605	-487
6	169*	85
7	474*	-328
8	267*	165
9	730	635
10	195*	-24
11	597	-694
12	97*	-188
13	414	391
15	295*	91
	6,6,L	
-15	548	604
-14	635	-509
-13	912	-820
-12	707	554
-11	1220	1175
-10	575	-476
-9	1352	-1369
-8	386	357

* These reflections were treated as unobserveds.

TABLE 5.7 page 8

	6,6,L	
-7	1535	1501
-6	963	-861
-5	1164	-1230
-4	1040	1089
-3	1106	1166
-2	1208	-1249
-1	1189	-1227
0	1133	1039
1	1632	1584
2	1151	-1005
3	1553	-1352
4	1040	811
5	1304	1066
6	1050	-994
7	1389	-1223
8	1034	958
9	1068	1116
10	814	-742
11	1016	-1022
12	416	536
13	797	855
14	251*	-275
15	538	-625
	7,6,L	
-15	132*	-124
-14	274*	-287
-13	454	426
-12	321*	288
-11	431	-494
-10	215*	-346
-9	326	453
-8	191*	40
-7	205*	-2
-6	186*	220
-5	502	-502
-4	335	421
-3	583	601
-2	447	-544
-1	155*	-211
0	328	381
1	196*	-161
2	159*	-78
3	565	467
4	263*	-176
5	463	-400
8	290*	-232
9	370*	244
11	239*	-200
12	413*	-300
13	237*	157
	8,6,L	
-15	533	547
-14	533	-452
-13	576	-549
-12	584	519
-11	954	881
-10	633	-552
-9	1015	-958
-8	503	446
-7	1340	1294
-6	760	-694
-5	1284	-1199
-4	911	940
-3	1533	1697
-2	1053	-1014
-1	1080	-1091
0	1132	970
1	740	718
2	1093	-1033
3	962	-867
4	1076	939
5	992	787
6	1056	-997
7	1210	-1090
8	694	621
9	1166	1181
10	702	-670
11	828	-841
12	498	431
14	315*	-246
	9,6,L	
-15	113*	-118
-13	454	481
-12	162*	120
-11	427	-466
-10	234*	-114
-9	404	390
-8	297*	173
-7	186*	-148
-6	363*	-142
-5	436	-482
-4	202*	330
-3	129*	71
-2	365	-435
-1	95*	32
0	219*	95
1	358*	-270
2	135*	80
3	254*	84
5	460*	140
7	277*	-215
9	211*	-26
10	274*	98
11	277*	205
12	151*	-173
13	180*	-24
	10,6,L	
-14	417	-431
-13	464	-460
-12	343	380
-11	488	345
-10	656	-597
-9	657	-693
-8	909	839
-7	984	941
-6	971	-839
-5	1372	-1315
-4	963	947
-3	1537	1622
-2	471	-450
-1	1235	-1187
0	636	658
1	961	942
2	891	-808
3	905	-758
4	1056	1007
5	797	682
6	1042	-959
7	1050	-981
8	657	658
9	1028	981
10	562	-505
11	719	-727
14	242*	-243
	11,6,L	
-13	47*	123
-12	324*	286
-11	178*	-8
-10	236*	-148
-9	124*	104
-8	208*	157
-7	423	-380
-5	320*	300
-4	360*	363
-3	267*	-243
-2	253*	-153
-1	151*	131
0	159*	125
1	373*	290
2	272*	-22
3	300*	-452
4	269*	249
5	296*	302
6	507	-496
7	295*	-300
8	361*	284
9	228*	-180
10	272*	92
11	188*	101
12	153*	-167
13	190*	-26
	12,6,L	
-11	595	534
-10	474	-461
-9	784	-703
-8	676	613
-7	871	836
-6	715	-614
-5	1115	-1116
-4	517	479
-3	1220	-1266
-2	620	-616
-1	1332	-1386
0	436	385
1	1179	1027
2	678	-529
3	1006	-991
4	837	724
5	1062	942
6	800	-639
7	934	-909
8	662	604
9	589	584
10	395	-466
	13,6,L	
-12	283*	170
-11	344*	243
-10	318*	-281
-9	295*	-229
-8	241*	227
-7	410	-355
-6	399	-252
-5	678	635
-4	287*	134
-3	323	-269
-2	131*	-124
-1	70*	188
0	210*	175
1	485	472
2	175*	-60
4	260*	95
6	228*	-72
7	304*	89
9	236*	-173
10	220*	64
11	182*	-25
12	143*	-63
	14,6,L	
-11	694	598
-10	645	-590
-9	733	-692
-8	578	486
-7	694	627
-6	388	-394
-5	651	-641
-4	490	484
-3	707	671
-2	773	-752
-1	869	-844
0	987	990
1	1006	987
2	806	-746
3	1036	-1017
4	675	546
5	884	910
6	303	-325
7	597	-641
8	58*	184
9	448	461
	15,6,L	
-9	205*	-164
-8	386	332
-3	335*	-271
-2	218*	-95
-1	281*	110
1	154*	50
3	319*	-146
4	84*	86
5	59*	57
6	208*	-24
7	238*	85
9	148*	80
11	246*	-167
	16,6,L	
-8	426	398
-7	521	504
-6	420	-454
-5	623	-522
-4	418	412
-3	646	590
-2	638	-593
-1	623	-656
0	775	855
1	793	755
2	561	-568
3	910	-906
4	450	404
5	807	782
6	153*	-186
7	622	-613
8	198*	116
9	436	523
10	146*	-304
	17,6,L	
-9	272*	134
-7	147*	-14
-6	225*	-119
-5	264*	-35
-4	164*	6
-3	164*	135
-2	193*	-207
-1	105*	117
0	333*	219
3	353	337
4	254*	76
5	74*	-96
7	180*	-107
8	236*	14
	18,6,L	
-4	410	456
-3	647	668
-2	441	-452
-1	611	-628
0	399	429
1	537	570
2	415	-389
3	516	-533
4	353	383
5	489	542
6	363	-399
	19,6,L	
-4	108*	145
-3	185*	194
-2	239*	-287
-1	150	-98
0	305	284
2	123*	-94
4	46*	-142
5	142*	-122
	20,6,L	
-3	518	523
	0,7,L	
1	229	276
2	359	-338
3	261*	-185
	1,7,L	
-3	228*	52
-2	1981	-2014
-1	483	-510
0	1797	1799
1	364	341
2	1950	-1845
3	385	-317
	2,7,L	
-3	209*	-69
-2	273*	77
-1	339	-285
0	273*	47
1	502	477
2	220*	-117
3	427	-445
	3,7,L	
-3	246*	-22
-2	1496	-1461
-1	216	-167
0	1883	1757
1	224	268
2	1833	-1571
3	370	-292
	4,7,L	
-2	412	-363
-1	232	-164
0	534*	309
1	146*	158
2	222*	49
	5,7,L	
-3	399	-346
-2	1060	-1203
-1	185*	30
0	1488	1370
2	1609	-1403
3	349	-279
	6,7,L	
-3	380	267
-2	480	-467
-1	157*	230
0	316*	197
1	363	-365
2	269*	203
3	433	451
	7,7,L	
-3	220*	-48
-2	975	-920
-1	376	376
0	1034	982
1	143*	-94
2	963	-866
3	256*	-19
	8,7,L	
-3	218*	-52
-2	230*	22
-1	217	199
0	418	-332
1	306	-319
2	272*	167
3	360	361
	9,7,L	
-3	373	287
-2	1041	-1064
-1	273	-352
0	1021	1099
1	183	139
2	751	-695
3	410	277
	10,7,L	
-3	403	-277
-2	243*	197
-1	213	224
0	286*	-10
1	141*	-121
2	229*	35
3	226*	75
	11,7,L	
-3	338*	194
-2	1112	-1400
-1	436	-518
0	1408	1497
1	209	234
2	1088	-1194
3	218*	32
	12,7,L	
-3	419	-395
-1	208	287
0	278*	54
	13,7,L	
-2	1111	-1085
-1	238	-250
0	1207	1348
	14,7,L	
-3	320	-248
-1	197*	48
0	259*	43
	15,7,L	
-2	785	-739
-1	177	136
0	939	923
	16,7,L	
-3	389*	-21
-2	205*	-242
	17,7,L	
-3	159*	-163
-2	746	-754
-1	110*	143
0	719	710
	18,7,L	
-3	188*	-81
-2	240	-301
-1	135	145
	0,8,L	
0	1525	1305
1	1201	-1164
2	1398	-1179
3	1178	1330
	1,8,L	
-3	221*	-172
-2	374	-340
-1	158*	-53
0	514	463
1	188*	18
2	389	-317
3	297*	-173

* These reflections were treated as unobserveds.

2,8,L

-3	1317	-1192
-2	1215	-1212
0	1386	1338
2	1318	-1156
3	1086	1029

3,8,L

-3	217*	-26
-2	437	-427
0	639	613
1	216*	-94
2	512	-451
3	217*	-67

4,8,L

-3	1099	-1050
-2	779	-685
-1	1176	1220
0	723	634
2	801	-649
3	915	982

5,8,L

-3	230*	-97
-1	387E	218
0	288*	89
2	229*	-57
3	221*	-9

6,8,L

-3	1154	-1024
-2	481	-484
-1	721	781
0	321*	255
1	723	-772
2	634	-555
3	956	1045

7,8,L

-3	222*	-20
-1	178*	-103
0	288*	-146
1	208*	88
2	229*	181
3	355	309

8,8,L

-3	1164	-1029
-2	584	-539
-1	606	663
0	598	514
1	534	-557
2	802	-731
3	749	760

9,8,L

-3	212*	16
-2	250*	124
0	299*	-309
1	127*	-138
2	288*	245
3	369	290

10,8,L

-3	1121	-1003
-2	803	-882
-1	661	781
0	761	775
1	636	-748
2	788	-715
3	968	850

11,8,L

-3	240*	17
-2	381	339
-1	148*	187
0	321*	-246
1	120*	-221
3	301	120

12,8,L

-3	686	-684
-2	875	-796
0	969	989

13,8,L

-3	193*	-81
-2	229*	2
-1	127*	20
0	246*	-20

14,8,L

-3	475	-438
-2	723	-722
-1	508	615
0	693	648

15,8,L

-3	201*	-202
-2	219*	-215
-1	170	177
0	214*	198

16,8,L

-3	598	-537
-2	477	-420
-1	454	478
0	427	348

17,8,L

-3	274	-305
-2	137*	-31
-1	109*	89

0,9,L

1	128*	89
3	232*	-169

1,9,L

-3	1187	-1206
-2	227*	71
-1	1342	1434
0	286*	-87
1	1195	-1237
2	235*	20
3	1184	1087

2,9,L

-3	382	-439
-2	230*	100
-1	465	454
0	314*	43
1	352	-418
2	227*	-96
3	214*	3

3,9,L

-3	1149	-1475
-2	226*	-7
0	438	-310
1	767	-797
2	429	483
3	1088	885

4,9,L

-3	220*	306
-2	225*	-9
0	283*	141
1	147*	-159
2	225*	-17
3	308*	151

5,9,L

-3	1075	-1105
-2	224*	34
-1	1221	1009
0	472	-416
1	655	-751
2	330	285
3	919	826

6,9,L

-3	257*	276
-2	221*	-33
0	278*	72
1	175*	-126
2	221*	-65
3	295	359

7,9,L

-3	1109	-1021
-2	238*	244
0	292*	-258
2	218*	113
3	1182	1045

8,9,L

-2	352*	227
0	284*	-275
2	213*	150
3	199*	132

9,9,L

-3	1078	-871
-2	432	369
0	286*	-214
3	1095	1165

10,9,L

-3	187*	60
-2	198*	123
-1	154*	-177
0	422	-343
2	472	309

11,9,L

-3	819	-695
-2	189*	215
0	273*	-208
3	896	981

12,9,L

-3	270*	-183
-2	177*	23
-1	221*	99
0	231*	-246

13,9,L

-3	752	-791
-2	239*	-83
-1	839	831
0	210*	-169

14,9,L

-3	371	-360
-2	148*	44
-1	281	318
0	272*	6

15,9,L

-3	704	-753
-2	142*	-131

0,10,L

0	1009	-909
1	441	-506
2	962	977
3	436*	303

1,10,L

-3	202*	-134
-1	207	-184
0	267*	-164
1	189	235
2	211*	66
3	283	-221

2,10,L

-3	917	-748
-2	951	869
-1	611	726
0	921	-899
1	348	-445
2	915	825
3	283*	123

3,10,L

0	262*	53
1	118*	14
2	208*	48
3	195*	130

4,10,L

-2	897	785
-1	652	667
0	801	-814
1	330	-389
2	753	726
3	204*	167

5,10,L

0	256*	145
1	114*	-211
3	309	306

6,10,L

-3	622	-502
-2	784	731
-1	509	559
0	925	-1024
1	437	-488
2	694	671
3	573	481

7,10,L

-3	593	480
-2	191*	-139
-1	157	-148
0	243*	69
1	168	-197
3	338	258

8,10,L

-3	199*	-121
-2	719	731
-1	332	317
0	886	-916
1	599	-664
2	811	819
3	908	875

9,10,L

-3	259	273
-2	210*	11
-1	118*	-251
1	183	-116
2	175*	-12

10,10,L

-3	221*	-52
-2	710	664
-1	170	140
0	676	-752
1	348	-470

11,10,L

-3	199*	-111
-2	201*	101
-1	118*	-18
0	199*	-98

12,10,L

-3	299	-225
-2	612	610
-1	239	200
0	606	-624

13,10,L

-3	128*	-74

0,11,L

1	152*	-23
3	167*	30

1,11,L

-3	288	279
-2	501	680
-1	332	-323
0	580	-544
1	414	494
2	645	576
3	627	-517

2,11,L

-3	170*	163
-2	401*	-54
-1	122*	-238
0	275*	247
1	206	201
2	276	-279

3,11,L

-3	346*	72
-2	1028	975
-1	229	-221
0	825	-840
1	226	285
2	636	608
3	544	-536

4,11,L

-3	231	153
-1	154	-302
1	156	148
2	413*	-20
3	159*	2

5,11,L

-3	162*	82
-2	929	920
-1	97*	-139
0	830	-931
1	124*	257
2	670	716
3	615	-421

6,11,L

-3	231*	180
0	202*	-143
3	147*	45

7,11,L

-3	332	221
-2	608	655
-1	86*	-109
0	798	-950
1	180	268
2	807	889
3	298	-225

8,11,L

-3	132*	64
1	81*	-167
2	151*	159
3	132*	66

9,11,L

-3	314	338
-2	492	570
-1	203	-249

10,11,L

-3	108*	-51

0,12,L

1	368	377
2	140*	143
3	637	-539

1,12,L

-1	467*	27
1	75*	-49
2	132*	-73
3	152*	-48

2,12,L

-3	706	728
-2	227*	148
1	398	495
3	784	-652

3,12,L

-2	193	-240
1	91*	-21
2	242	-280
3	115*	29

4,12,L

-3	739	702

* These reflections were treated as unobserveds.

CONCLUSION

The work reported in Chapters 2 and 4 strongly suggests that the reaction of all platinum and palladium dithioacid compounds with tertiary phosphines occurs through stepwise cleavage of the metal-sulphur bonds of one of the dithio-chelate rings, generating four coordinate complexes in all cases. With 1:1 molar ratios of tertiary phosphines the four coordinate complex $M(S\text{-}S)_2PR'_3$ is produced [$(S\text{-}S)^- = {}^-S_2PR_2$, ${}^-S_2CNR_2$, ${}^-S_2COR$, ${}^-S_2P(OEt)_2$], which contains bidentate and unidentate dithio-ligands. Confirmation of this type of structure in the solid state was obtained from x-ray studies of $Pd(S_2PPh_2)_2PPh_3$ and $Pt(S_2CNEt_2)_2PPh_3$ (Chapters 3 and 5 respectively). Although no studies of the reactions of the dithiocarboxylates have been made in this work a similar structure has been found in Pt(p-dithiocumato)$_2$PPh$_2$Me [70] suggesting that these compounds also conform to the general pattern.

Further treatment with an excess of tertiary phosphine completes the cleavage of the chelate ring, giving the four coordinate complex $[M(S\text{-}S)(PR'_3)_2](S\text{-}S)$ in the first instance. The crystal structure of $[Pd(S_2PPh_2)(PEt_3)_2]S_2PPh_2$ [58] confirms the presence of ionic and bidentate dithio-ligands in the solid state. For $(S\text{-}S)^- = {}^-S_2PR_2$ (R = Me, Et, Ph and probably F) these ionic 1:2 compounds rapidly revert to the 1:1 compounds in non polar solvents by means of nucleophilic attack by ${}^-S_2PR_2$ on the metal. Similar processes occur for ${}^-S_2P(OEt)_2$, ${}^-S_2COR$ and ${}^-S_2CNR_2$ but in addition competing nucleophilic attacks may occur. Thus the

products $(PR'_3)_2MS_2P(O)OEt$ and $(PR'_3)_2MS_2CO$ may be obtained from the $^-S_2P(OEt)_2$ and ^-S_2COR complexes respectively by nucleophilic attack by the anion on a coordinated alkoxy group in the bidentate ligand. In the case of the $^-S_2CNR_2$ complex, the presence of free PR'_3 catalyses the competing nucleophilic attack by $^-S_2CNR_2$ on chlorinated solvents.

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ACKNOWLEDGEMENTS

I wish to thank my two supervisors Dr. T. A. Stephenson and Dr. R. O. Gould for their constant assistance and advice over the years. I am grateful to the University of Maryland for the use of the XRAY crystallographic programs, to the Edinburgh Regional Computing Centre for the use of their facilities, and to the Science Research Council for a grant. Finally, I should like to thank my parents and my husband for their continual help and encouragement, and my typist Mrs. A. Lang for her cheerful patience.

Tertiary Phosphine Complexes of Bis(diphenylphosphinodithioato)palladium(II). A Correction

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Reprinted from

Chemical Communications 1970

The Chemical Society, Burlington House, London W1V OBN

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By (Miss) J. M. C. ALISON and T. A. STEPHENSON*
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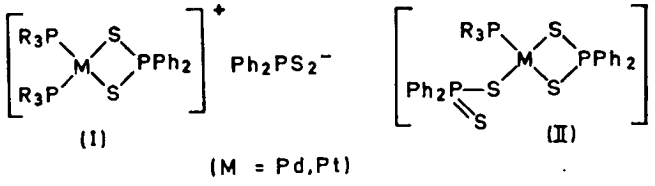
Summary The 1 : 1 and 1 : 2 tertiary phosphine adducts of $Pd(S_2PPh_2)_2$, originally formulated as five- and six-co-ordinate complexes, respectively, are probably both four-co-ordinate.

RECENTLY evidence was reported for 1 : 1 and 1 : 2 tertiary phosphine adducts of $Pd(S_2PPh_2)_2$ which were tentatively formulated as five- and six-co-ordinate complexes, respectively.[1] Further work on these and the isomorphous platinum(II) complexes has now indicated that this formulation is incorrect and that the "six-co-ordinate" complexes are in fact four-co-ordinate ionic species (I) and the "five-co-ordinate" complexes are probably the four-co-ordinate species (II).



The evidence for the revised structures is as follows:

(a) As discussed previously,[1] the 1 : 2 complexes rapidly dissociate to 1 : 1 complexes in benzene and carbon disulphide. However, in more polar solvents such as dichloromethane the 1 : 2 complexes are stabilized and conductivity measurements (Table 1) are consistent with those expected for 1 : 1 electrolytes in this solvent.

TABLE 1

Equivalent conductivities (25°) *of some* 1 : 1 *and* 1 : 2 *complexes in* CH_2Cl_2

Compound	Concn. (10^{-4}M)	Λ^a	Λ^a (plus excess of PR_3)
$Bu^n_4NClO_4$	10·1	22·7	—
$Pd(S_2PPh_2)_2(PEt_3)_2$ ..	8·3	25	—
$Pd(S_2PPh_2)_2(PMe_2Ph)_2$ ..	12	24·4	—
$Pd(S_2PPh_2)_2(PMe_2Ph)$ ..	13·7	2·5	26·4
$Pt(S_2PPh_2)_2(PPh_3)_2$	8·8	26·6	—
$Pt(S_2PPh_2)_2(PPh_3)$	9·4	0·72	32·35
$Pt(S_2PPh_2)_2(PMePh_2)_2$ ..	8·6	30·2	—
$Pt(S_2PPh_2)_2(PMePh_2)$ ..	8·1	1·18	29·77

[a] $cm^2\ ohm^{-1}mole^{-1}$.

(b) Addition of an excess of tertiary phosphine to the 1 : 1 complexes (non-electrolytes) in CH_2Cl_2 produces an increase in conductivity consistent with the formation of 1 : 1 electrolytes (Table 1).

(c) ^1H n.m.r. data on 1 : 2 platinum(II) complexes of $MePh_2P$ and Me_2PhP in deuteriochloroform (Table 2) indicate a *cis*-arrangement of tertiary phosphine groups (no virtual coupling[2]).

(d) An *X*-ray structural analysis[3] on $[Pd(S_2PPh_2)_2(PEt_3)_2]$ is sufficiently advanced to verify the authenticity of structure (I). The mull and solution i.r. spectra of these 1 : 2 complexes are identical, suggesting the same species is retained in solution, and this is supported by ^1H n.m.r. and conductimetric data.

The reformulation of the 1 : 2 complexes as the ionic species (I) and their ready interconversion with the 1 : 1 complexes casts doubt on the validity of the five-co-ordinate structure postulated earlier for the latter.[1] No direct evidence is yet available to support (II) (a crystal structure of $[Pd(S_2PPh_2)_2(PPh_3)]$ is in progress) but an analogous structure has been postulated by Tebbe and Muetterties[4] for 1 : 1 tertiary phosphine complexes of palladium(II) difluorodithiophosphate on the basis of i.r. and ^{19}F n.m.r. evidence.

TABLE 2

^1H *n.m.r. data* (*methyl region*) *for some platinum tertiary phosphine complexes in* $CDCl_3$

Compound	τ value[a]	Multiplicity and J value (Hz)[b]
$[Pt(S_2PPh_2)_2(PMe_2Ph)_2]$	8·27	three doublets J(P–H) 12·6, J(Pt–H) 49
$[Pt(S_2PPh_2)_2(PMePh_2)_2]$	7·99	three doublets J(P–H) 13·2, J(Pt–H) 49·5
$[Pt(S_2PPh_2)_2(PMePh_2)]$	7·67	three doublets J(P–H) 11·3, J(Pt–H) 37·5

[a] ±0·01. [b] J(P–H) ± 0·2 Hz; J(Pt–H) ± 0·5 Hz.

If (II) is correct, the best explanation for the "isomers" of $[Pd(S_2PPh_2)_2PPh_3]$[1] is probably different orientations of the unidentate diphenylphosphinodithioato-group with respect to the bulky triphenylphosphine ligand.

Finally, preliminary studies on tertiary phosphine complexes of platinum(II) dithiocarbamates[5] suggest that 1 : 1 and 1 : 2 adducts with analogous structures to (I) and (II) are formed.

We thank the Science Research Council for an award (to J.M.C.A.) and Johnson-Matthey Limited for a loan of palladium(II) chloride.

(*Received, June* 22*nd*, 1970; *Com.* 984.)

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[5] J. P. Fackler, jun., J. A. Fetchin, and W. C. Seidel, *J. Amer. Chem. Soc.*, 1969, **91**, 1217 and references therein.

Metal Complexes of Sulphur Ligands. Part II.[1,2] Reaction of Bis(diphenylphosphinodithioato)-platinum(II) and -palladium(II) with Ligands Containing Group V_B Atoms

By (Miss) J. M. C. Alison, T. A. Stephenson,* and (in part) R. O. Gould, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reprinted from

JOURNAL
OF
THE CHEMICAL SOCIETY

SECTION A
Inorganic, Physical, and Theoretical Chemistry

1971

Metal Complexes of Sulphur Ligands. Part II.[1,2] Reaction of Bis(diphenylphosphinodithioato)-platinum(II) and -palladium(II) with Ligands Containing Group VB Atoms

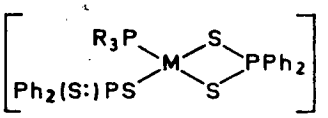
By (Miss) J. M. C. Alison, T. A. Stephenson,* and (in part) R. O. Gould, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Reaction of $Pt(S_2PPh_2)_2$ with tertiary phosphines (PPh_3, $PMePh_2$, PMe_2Ph) gives crystalline 1 : 1 and 1 : 2 adducts. With triphenylarsine or triphenylstibine, only 1 : 1 adducts can be isolated and with pyridine, i.r. evidence indicates that the 1 : 1 adduct is only stable in solution in the presence of an excess of pyridine. As reported earlier for the analogous palladium compounds, the 1 : 2 adducts rapidly dissociate to the 1 : 1 compounds in non-polar solvents (benzene or carbon disulphide); however, it is now found that they can be stabilised in more polar solvents (dichloromethane or nitromethane). Conductivity measurements in the latter suggests all these 1 : 2 adducts have a four-co-ordinate ionic structure and this is confirmed by an *X*-ray analysis of $[Pd(S_2PPh_2)(PEt_3)_2]S_2PPh_2$. An *X*-ray analysis on $[Pd(S_2PPh_2)_2(PPh_3)]$ suggests a four-co-ordinate monomeric structure for the 1 : 1 compounds with uni- and bi-dentate co-ordination of dithioacid ligands. Finally, an empirical i.r. method for distinguishing unidentate, bidentate, and ionic modes of co-ordination of the diphenylphosphinodithioato-group to platinum and palladium is discussed.

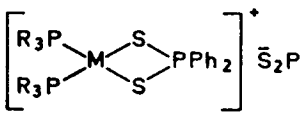
RECENTLY, one of us reported[2] that the compound $Pd(S_2PPh_2)_2$ reacted with tertiary phosphines to give both 1 : 1 and 1 : 2 adducts. On the basis of i.r. studies, interpreted by analogy with earlier studies on 1 : 1 and 1 : 2 Lewis base adducts with palladium carboxylates,[3] these dithioacid complexes were tentatively formulated as examples of five- and six-co-ordinate palladium(II) respectively. The former was consistent with earlier studies by Fackler *et al.*[4] on the reactions of other palladium (and platinum) dithioacid complexes $M(S{-}S)_2$ [M = Pd or Pt; $(S{-}S)^- = RCS_2^-$, $ROCS_2^-$, $Et_2NCS_2^-$, and $(EtO)_2PS_2^-$] with methyldiphenylphosphine, in which 1 : 1 adducts were characterised and formulated as five-co-ordinate compounds on the basis of ^1H n.m.r. studies. A brief mention was also made of the precipitation from solution of what may be six-co-ordinate species when an excess of methyldiphenylphosphine was added to platinum(II) compounds of ring substituted dithiobenzoates, but no details were given.

Here, additional evidence is presented which shows that the above interpretation is incorrect and that the 1 : 1 and 1 : 2 tertiary phosphine adducts of $Pd(S_2PPh_2)_2$ should be reformulated as the four-co-ordinate compounds (I) and (II) respectively. In addition, the results of a detailed investigation of the reaction of ligands containing Group VB atoms with the isomorphous $Pt(S_2PPh_2)_2$ are presented. These lend support to the conclusions drawn from the palladium study. Analogous structures have also recently been postulated by Tebbe and Muetterties[5] for tertiary phosphine complexes of palladium(II) difluorodithiophosphate on the basis of i.r. and ^{19}F n.m.r. studies.

In Part III of this series,[6] the results of a re-investigation of the reactions between tertiary phosphines and platinum(II) dithiocarbamates, xanthates, and dithiophosphates will be discussed. The evidence strongly suggests that reactions of all platinum (and palladium) dithioacid compounds with tertiary phosphines can be rationalised in terms of the formation and, in the case of xanthate and dithiophosphate, of the rearrangment reactions of four-co-ordinate 1 : 1 and 1 : 2 adducts of type (I) and (II) respectively.



(I)



(II)

RESULTS AND DISCUSSION

Reaction of either potassium tetrachloroplatinate(II) or platinum(II) acetate with a six-fold excess of diphenylphosphinodithioic acid readily gives orange-red crystals of $Pt(S_2PPh_2)_2$. This compound is isomorphous with the corresponding palladium and nickel salts (*X*-ray structural analysis of the latter[7] confirms the structure is a square planar monomer), the mass spectrum at 150° shows the highest group of peaks corresponds to $Pt(S_2PPh_2)_2^+$ and the i.r. spectra (800—400 cm^{-1}) of the three compounds are almost identical. The compounds are non-conducting in dichloromethane.

Reaction of a suspension of $Pt(S_2PPh_2)_2$ in benzene with tertiary phosphines (1 : 1 molar ratios) rapidly gives bright yellow solutions, from which lemon-yellow compounds of stoicheiometry $[Pt(S_2PPh_2)_2PR_3]$ (PR_3 = PPh_3, $PMePh_2$, and PMe_2Ph) can be isolated, either by

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[2] Part I, T. A. Stephenson and B. D. Faithful, *J. Chem. Soc.* (*A*), 1970, 1504.
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[5] F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, 1970, **9**, 629.
[6] Miss J. M. C. Alison and T. A. Stephenson, to be published.
[7] P. Porta, A. Sgamellotti, and N. Vinciguerra, *Inorg. Chem.*, 1968, **7**, 2625.

precipitation with light petroleum or by removal of solvent under reduced pressure. Molecular weight measurements in chloroform show them to be monomeric. The ^1H n.m.r. spectra of $[Pt(S_2PPh_2)_2(PR_3)]$ (PR_3 = $PMePh_2$ or PMe_2Ph) (Table 1) in carbon disulphide or deuteriochloroform consists, in the methyl region, of a triplet of doublets which confirms direct co-ordination of the tertiary phosphine to platinum, rather than reaction with the dithio-ligand. For comparison, the chemical shifts and coupling constants of methyldiphenylphosphine adducts of other platinum dithioacids are given in Table 1. The close similarity of these

TABLE 1

^1H N.m.r. data [methyl region (phos)] for some platinum and palladium tertiary phosphine complexes at 301 K

Compound	Solvent	τ Value [a]	Multiplicity and J values [b] J(P–H)	J(Pt–H)
$[Pt(S_2PPh_2)_2(PMePh_2)]$	CS_2	7·69	11·4	38·0
$[Pt(S_2PPh_2)_2(PMePh_2)]$	$CDCl_3$	7·67	11·3	37·5
$[Pt(S_2CNEt_2)_2(PMePh_2)]$ [c]	$CDCl_3$	7·72	10·0	38·0
$[Pt(S_2COEt)_2(PMePh_2)]$ [c]	$CDCl_3$	7·80	11·0	41·0
$[Pd(S_2PPh_2)_2(PMePh_2)]$	CS_2	7·68 [d]	11·2	
$[Pt(S_2PPh_2)_2(PMe_2Ph)]$	CS_2	8·08	11·3	38·0
$[Pt(S_2PPh_2)(PMePh_2)_2]$-$S_2PPh_2$	$CDCl_3$	7·99	13·2	49·5
$[Pt(S_2PPh_2)(PMe_2Ph)_2]$-$S_2PPh_2$	$CDCl_3$	8·27	12·6	49·0
$[Pt(S_2PPh_2)(PMe_2Ph)_2]$-$BPh_4$	$CDCl_3$	8·66	10·0	39·0

[a] ±0·01. [b] Multiplicity: three doublets except where stated otherwise, J(P–H) ± 0·2 Hz; J(Pt–H) ± 0·5 Hz. [c] From J. P. Fackler, jun., W. C. Seidel, and J. A. Fetchin, *J. Amer. Chem. Soc.*, 1968, **90**, 2707. [d] One doublet.

with that of $[Pt(S_2PPh_2)_2(PMePh_2)]$ is consistent with a similar structure for all these 1 : 1 adducts.

With triphenylphosphine, a similar phenomenon is observed to that found with $Pd(S_2PPh_2)_2$.[2] Precipitation of the triphenylphosphine complex at room temperature gives a bright yellow crystalline solid. However, precipitation at low temperature (*ca.* 200 K) gives a pale yellow powder. The mull i.r. spectra and m.p.s of these compounds are different but the solution i.r. spectra (benzene or carbon disulphide) are identical. Both compounds analyse for $[Pt(S_2PPh_2)_2(PPh_3)]$ and unlike the palladium system,[2] the low temperature form does not change to the bright yellow form in the solid phase. However, this change does occur when the former is dissolved in benzene and reprecipitated at room temperature. Clearly, these observations are consistent with the presence of isomers but speculation on the structure of these isomers is deferred until the section on i.r. studies.

Reaction of $Pt(S_2PPh_2)_2$ with an excess of triphenylarsine and triphenylstibine in benzene also gives the 1 : 1 adducts $[Pt(S_2PPh_2)_2(LPh_3)]$ (L = As or Sb), although attempts to obtain a different low temperature form have been unsuccessful. In contrast to the phosphine complexes, which are stable in benzene, carbon disulphide, and dichloromethane (non-conducting in the latter, see Table 2), the arsine complex, in solution, slowly reverts to $Pt(S_2PPh_2)_2$ and triphenylarsine whereas, in the absence of an excess of triphenylstibine, the stibine complex immediately dissociates in solution. Reaction of $Pt(S_2PPh_2)_2$ with an excess of pyridine in carbon disulphide gives a lemon-yellow solution but attempts to isolate a solid complex only resulted in recovery of the starting material. However, on the basis of solution i.r. studies (see later) there is probably a 1 : 1 adduct present in solution. In contrast, there is no reaction under any conditions between $Pd(S_2PPh_2)_2$ and triphenylarsine, triphenylstibine, or pyridine. With $Ni(S_2PPh_2)_2$, an excess of pyridine readily gives the green, crystalline 1 : 2 adduct $[Ni(S_2PPh_2)_2(C_5H_5N)_2]$. A very recent *X*-ray structural analysis [8] has shown this to be an octahedral complex with a *trans*-arrangement of pyridine ligands and bidentate diphenylphosphinodithioato-groups.

If, however, a suspension of $Pt(S_2PPh_2)_2$ in benzene is shaken with an excess of any tertiary phosphine, the initial yellow solution rapidly becomes colourless and removal of solvent under reduced pressure gives white powders of stoicheiometry $[Pt(S_2PPh_2)_2(PR_3)_2]$ (PR_3 = PPh_3, $PMePh_2$, or PMe_2Ph). This is to be contrasted with the behaviour of $Pd(S_2PPh_2)_2$, which forms 1 : 2 adducts in benzene solution with PEt_3, PMe_2Ph, and $PMePh_2$ but not with $PEtPh_2$ or PPh_3.[2] As reported earlier for the palladium complexes,[2] the platinum 1 : 2 adducts are also unstable in non-polar solvents such as benzene and carbon disulphide, readily dissociating to the 1 : 1 complexes. This process can be monitored by watching the growth in the i.r. spectrum of a band characteristic of the 1 : 1 adduct (*ca.* 540 cm^{-1}) and the loss of one characteristic of the 1 : 2 compound (*ca.* 560 cm^{-1}). As in the case of the palladium complexes, only the addition of an excess of tertiary phosphine can partially stabilise the 1 : 2 adducts in these solvents.

However, in more polar solvents such as chloroform, dichloromethane, and nitromethane, the platinum 1 : 2 adducts are stabilised. The mull and solution i.r. spectra are identical, suggesting that the same species is retained in these solvents and, on removal of solvent, the 1 : 2 compound is recovered. Furthermore, conductivity measurements in dichloromethane and nitromethane (Table 2), both on the 1 : 2 compounds and on the 1 : 1 compounds plus an excess of phosphine, are consistent with those expected for 1 : 1 electrolytes. In addition, a molecular weight determination of $[Pt(S_2PPh_2)(PMe_2Ph)_2]S_2PPh_2$ in chloroform gives a value of half that required for a monomeric complex, indicating a 1 : 1 electrolyte in this solvent.

It is interesting to note that although no evidence is found for the formation of $[Pt(S_2PPh_2)(AsPh_3)_2]S_2PPh_2$ in benzene solution, addition of an excess of triphenylarsine to a dichloromethane solution of $[Pt(S_2PPh_2)_2(AsPh_3)]$ produces a lightening of colour and an appreciable increase in conductivity (Table 2). The

[8] P. Porta, A. Sgamellotti, and N. Vinciguerra, *Inorg. Chem.*, 1971, **10**, 3.

maximum value of $\Lambda_{0\cdot001M}$ found (*ca.* 11) would suggest *ca.* 30—40% conversion into an ionic species in this solvent. However, on removal of solvent, the i.r. spectrum of the residue contains no band at *ca.* 560 cm^{-1} and the compound on dissolution is non-conducting. Clearly, the triphenylarsine 1 : 2 adduct is only partially stabilised in fairly polar solvents.

TABLE 2

Equivalent conductivities (298 K) of some platinum and palladium 1 : 1 and 1 : 2 complexes

Solvent	Compound	Concn. (10^{-4}M)	Λ [a]	Λ [a] plus excess of PR_3
CH_2Cl_2	Ph_4AsCl,HCl	9·8	55·3	
	$Bu^n_4NClO_4$	10·1	22·7	
		3·1	32·1	
	$Pt(S_2PPh_2)_2$	8·8	0·09	
	$[Pt(S_2PPh_2)_2(PPh_3)]$	9·4	0·72	32·3
	$[Pt(S_2PPh_2)_2(PMePh_2)]$	8·1	1·2	29·8
	$[Pt(S_2PPh_2)_2(PMe_2Ph)]$	12·1	0·63	23·0
	$[Pt(S_2PPh_2)_2(AsPh_3)]$	8·6	0·21	10·9 [b]
	$[Pt(S_2PPh_2)(PPh_3)_2]S_2PPh_2$	8·8	26·6	
	$[Pt(S_2PPh_2)(PMePh_2)_2]$-$S_2PPh_2$	8·6	30·2	
	$[Pt(S_2PPh_2)(PMe_2Ph)_2]$-$S_2PPh_2$	12·0	33·2	
	$[Pt(S_2PPh_2)(PMe_2Ph)_2]BPh_4$	9·2	33·6	
	$[Pt(S_2PPh_2)(PMe_2Ph)_2]Cl$	8·4	41·9	
	$[Pt(diphos)_2](S_2PPh_2)_2$	1·7	21·7	
	$[Pt(diphos)_2](BPh_4)_2$	1·4	31·2	
	$[Pd(S_2PPh_2)_2(PPh_3)]$	8·8	0·64	19·2
	$[Pd(S_2PPh_2)_2(PEtPh_2)]$	15·7	1·8	20·0
	$[Pd(S_2PPh_2)_2(PMe_2Ph)]$	13·7	2·5	26·4
	$[Pd(S_2PPh_2)_2(PMePh_2)]$	10·0	1·5	31·6
	$[Pd(S_2PPh_2)(PMe_2Ph)_2]$-$S_2PPh_2$	12·0	24·4	
	$[Pd(S_2PPh_2)(PMePh_2)_2]$-$S_2PPh_2$	5·5	16·8	
	$[Pd(S_2PPh_2)(PEt_3)_2]S_2PPh_2$	8·3	25·0	
	$[Pd(diphos)_2](S_2PPh_2)_2$	4·1	36·8	
CH_2Cl_2–pyridine	$[Ni(S_2PPh_2)_2(C_5H_5N)_2]$	17·8	1·7	
CH_3NO_2	$[Pt(diphos)_2](S_2PPh_2)_2$	1·4	66·6	
	$[Pd(diphos)_2](S_2PPh_2)_2$	2·6	74·7	
	$[Pd(S_2PPh_2)(PMePh_2)_2]$-$S_2PPh_2$	4·8	42·0	
	$[Pd(S_2PPh_2)_2(PMePh_2)]$	11·4	8·3	53·0

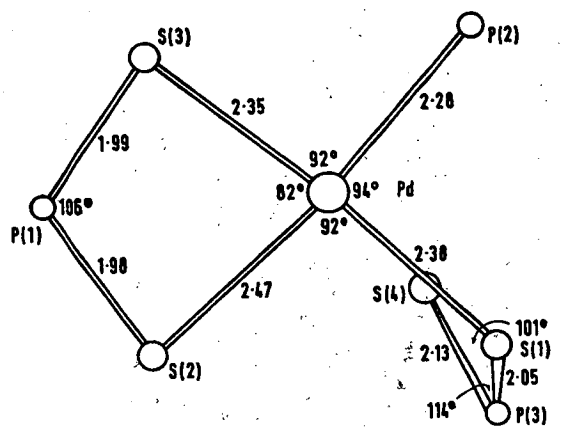
[a] In S cm^2 mol^{-1}. [b] Addition of excess $AsPh_3$.

The ^1H n.m.r. data for $[Pt(S_2PPh_2)(PR_3)_2]S_2PPh_2$ (PR_3 = PMe_2Ph or $PMePh_2$) (Table 1) are very similar to those of the 1 : 1 compounds, although the coupling constants are slightly larger and the methyl resonances occur at a slightly higher field.

Similarly, conductivity measurements on the palladium complexes (Table 2) confirm the ionic nature of the 1 : 2 adducts. The palladium compounds (PEt_3, PMe_2Ph, and $PMePh_2$) are completely stabilised in nitromethane; in dichloromethane and chloroform they are slightly dissociated, as shown by the presence of a weak band at *ca.* 540 cm^{-1} (*cf.* the corresponding platinum compounds, which are completely stabilised in these solvents). Furthermore, although there is no evidence for the formation of palladium 1 : 2 complexes of PPh_3 or $PEtPh_2$ in benzene solution,[2] addition of an excess of these phosphines to dichloromethane solutions of the corresponding 1 : 1 adducts produces a lightening of colour and an increase in conductivity (Table 2). The values of Λ found indicate an appreciable amount of an ionic species is present. However, although the solution i.r. spectra of these mixtures contain a weak band at *ca.* 560 cm^{-1}, all attempts to isolate an ionic species gave only the 1 : 1 compounds.

Thus, the non-electrolyte six-co-ordinate structure suggested earlier [2] must be discarded and the 1 : 2 adducts of both palladium and platinum reformulated on the evidence given here as the four-co-ordinate ionic compounds (II). Confirmation of the authenticity of structure (II) has now been established by means of a two-dimensional *X*-ray diffraction study on $[Pd(S_2PPh_2)(PEt_3)_2]S_2PPh_2$.[9]

The reformulation of the 1 : 2 compounds as the ionic species (II) and their ready interconversion with the 1 : 1 complexes casts doubt on the validity of the five-co-ordinate structure postulated earlier [2] for the latter. An *X*-ray structural analysis of $[Pd(S_2PPh_2)_2(PPh_3)]$ is now sufficiently advanced [10] to verify the unusual structure (I) containing four-co-ordinate palladium and bidentate and unidentate diphenylphosphinodithioato-groups. The Figure shows the square-planar arrangement about the palladium atom and the distinction between the unidentate and bidentate ligands. The non-co-ordinating sulphur atom, S(4), is 3·3 Å below the plane, and more than 3·5 Å from the palladium atom.



The heavy atoms of bis(diphenylphosphinodithioato)triphenylphosphinepalladium(II) projected into the best plane of Pd, S(1), S(2), S(3), P(1), and P(3); bond lengths and angles are shown

Infrared Spectra.—In an earlier paper,[2] the mode of bonding of the diphenylphosphinodithioato-ligand to palladium was inferred from the position and separation of the asymmetric (ν_1) and symmetric (ν_2) PS_2^- stretching frequencies. At the time, it was considered that this approach was valid and completely analogous to the situation found in carboxylate complexes.[3,11] However, such an approach is now considered unsuitable in view of the fact that, in the $Ph_2PS_2^-$ group,

[9] C. A. Beevers and A. Fraser, to be published.
[10] Miss J. M. C. Alison and R. O. Gould, to be published.
[11] For references and discussion see K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' p. 222 *et seq.*, 2nd edn., Wiley, New York and London, 1969.

the similar energies of ν_1 and ν_2 to the many other vibrations of the same symmetry class will surely lead to extensive coupling of these vibrations. This in turn will invalidate any arguments based on the expected shifts of uncoupled νPS_2^- vibrations with changes in the mode of co-ordination.

Nevertheless, careful examination of the i.r. spectra of these platinum and palladium complexes (these are reproduced from 800 to 250 cm^{-1} in the Experimental section) suggest that the presence of certain bands appears to be diagnostic of unidentate, bidentate, and ionic co-ordination of the diphenylphosphinodithioate group to these metals. For the reason given above, no attempt has been made to assign these characteristic bands to any specific mode of vibration, although it is suggested that they probably contain an appreciable contribution from PS_2^- stretching frequencies. In Table 3, the two characteristic bands are given for each mode of bonding. In addition, the Table contains a number of examples taken from these studies, in order

TABLE 3

Characteristic bands for determining the mode of co-ordination of the diphenylphosphinodithioate group to palladium(II) and platinum(II) ions

Compound	Uni-dentate [a]	Bi-dentate [b]	Ionic [c]
$[Pt(Pd)(S_2PPh_2)_2(PMe_2Ph)]$	645, 539	603, 571	
$[Pt(S_2PPh_2)_2(AsPh_3)]$	645, 539	603, 571	
$[Pt(S_2PPh_2)_2(SbPh_3)]$	643, 539	603, 572	
$[Pt(S_2PPh_2)_2(PPh_3)]$ (bright yellow)	645, 539	603, 571	
$[Pt(S_2PPh_2)_2(PPh_3)]$ (pale yellow)	648, 540	603, 570	
$[Pd(S_2PPh_2)(PEt_3)_2]S_2PPh_2$		605, 573	650, 560
$[Pt(Pd)(S_2PPh_2)(PMePh_2)_2]S_2PPh_2$		603, 571	655, 562
$[Pt(Pd)(S_2PPh_2)(PMe_2Ph)_2]S_2PPh_2$		603, 570	656, 562
$[Pt(S_2PPh_2)(PMe_2Ph)_2]BPh_4$		603, 573	
$[Pt(S_2PPh_2)(PMe_2Ph)_2]Cl$		603, 573	
$[Pt(Pd)(diphos)_2](S_2PPh_2)_2$			650, 563
$[Pt(diphos)_2](BPh_4)_2$			

[a] *Cf.* Ph_2PS_2H 638 and 540 cm^{-1}. [b] *Cf.* $Pt(S_2PPh_2)_2$ 601 and 567 cm^{-1}. [c] *Cf.* $Cs(S_2PPh_2)$ 654 and 562 cm^{-1}.

that the usefulness of these characteristic bands for structure determination might be illustrated. A convincing test of the validity of these assignments is provided by the syntheses of $[Pt(S_2PPh_2)(PMe_2Ph)_2]X$ ($X^- = Cl^-$, or BPh_4^-), where the i.r. spectra contain 'bidentate' but not 'ionic' bands (Table 3).

The product from reaction of $M(S_2PPh_2)_2$ (M = Pt or Pd) with excess 1,2-bis(diphenylphosphino)ethane ($Ph_2PCH_2CH_2PPh_2$ = diphos) provides an excellent example of the use of these characteristic bands in determining structural details. The white products analyse for $[M(S_2PPh_2)_2(diphos)_2]$ and the i.r. spectra (Table 3) contain only 'ionic' bands, suggesting the compounds should be formulated as $[M(diphos)_2](S_2PPh_2)_2$. This is confirmed by conductivity measurements (Table 2) and by synthesis of $[Pt(diphos)_2](BPh_4)_2$ with consequent disappearance of the 'ionic' bands. Similarly, the solution i.r. spectrum of $Pt(S_2PPh_2)_2$ and excess pyridine in carbon disulphide shows bands at 573 and 540 cm^{-1}, indicating the presence of a 1 : 1 complex of type (I).

Although the two isomers of $[M(S_2PPh_2)_2PPh_3]$ (M = Pd or Pt) have different mull i.r. spectra, the differences stem from changes in the region *ca.* 500 and 700 cm^{-1} (see reference 2 for details of the palladium compounds). The characteristic bands of 'bidentate' and 'unidentate' co-ordination remain unchanged (Table 3). Therefore, it is suggested that the best explanation for the isomers of $[M(S_2PPh_2)_2PPh_3]$ is probably different orientations of the unidentate diphenylphosphinodithioate-group with respect to the bulky triphenylphosphine ligand. This is expected to produce changes in the i.r. spectra in regions associated with phenyl vibrations of both tertiary phosphine and dithio-ligand (*ca.* 500 and 700 cm^{-1}) but little change in the vibrations associated with the actual mode of bonding. Clearly, there is no need to invoke a five-co-ordinate low-temperature form to explain the spectral changes. Unfortunately, the low-temperature platinum isomer is not sufficiently crystalline for *X*-ray analysis and therefore direct proof of this theory is not possible.

Dissolution of either isomer in carbon disulphide gives identical i.r. solution spectra. These are very similar to that of the mull spectrum of the low temperature form, except for the additional weak band in the former at 673 cm^{-1} (palladium [2]) and 675 cm^{-1} (platinum), the intensity of which increases with concentration. A possible explanation for these observations is that solvation of a common intermediate occurs in solution. This intermediate is very similar in structure to the low-temperature isomer which is formed on removal of solvent. Apparently, the latter is kinetically inert for platinum, but rapidly converts to the room-temperature form for palladium.

Finally it should be noted that for $[Ni(S_2PPh_2)_2(C_5H_5N)_2]$ the 'bidentate' bands occur at 632 and 570 cm^{-1}. Similarly, preliminary studies on diphenylphosphinodithioato-complexes of rhodium, ruthenium, and osmium [12] indicate, in certain instances, some variation in the higher-energy band positions compared to those given in Table 3. However, in all compounds examined to date, the lower energy band positions are very similar to those given in Table 3. By analogy with carboxylate complexes, where ν_1 is much more sensitive to changes in the metal than ν_2,[11] this might suggest that the higher energy band possesses appreciable ν_1 character and the lower ν_2 character.

In spite of these variations, it is hoped that this diagnostic method will prove invaluable in future studies, both for analysing the structure of diphenylphosphinodithioate complexes and for following the structural interconversions which are a feature of the dithioacid complexes so far considered.

EXPERIMENTAL

Microanalyses were by the Analytical Laboratory, Edinburgh University, and by A. Bernhardt, West Germany.

[12] D. J. Cole-Hamilton and T. A. Stephenson, unpublished work.

Molecular weights were determined in dry ethanol-free chloroform at 37° on a Mechrolab Osmometer (model 301A), calibrated with benzil. I.r. spectra were recorded in the region 4000—250 cm^{-1} on a Perkin-Elmer model 457 and 225 Spectrometer using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. Spectra are listed for each compound (800—250 cm^{-1}). Conductivity measurements were made on a model 310 Portland Electronics conductivity bridge. N.m.r. spectra were obtained on a Perkin-Elmer model RS10 60 MHz spectrometer and a Varian Associates HA100 spectrometer. Mass spectra were measured on an AEI MS20 spectrometer. M.p.s were determined with a Kofler hot-stage microscope and are uncorrected.

Materials.—Palladium(II) chloride and potassium tetrachloroplatinate(II) (Johnson–Matthey); triphenylphosphine and dimethylphenylphosphine (B.D.H.), triphenylarsine (Emanuel), triphenylstibine (Koch–Light), triethylphosphine (B. Newton Main); ethyldiphenylphosphine and methyldiphenylphosphine were prepared by the Grignard method. Diphenylphosphinodithioic acid and its caesium salt were prepared as described previously.[2]

Platinum Compounds

Bis(diphenylphosphinodithioate)platinum(II).— Potassium tetrachloroplatinate(II) (1·81 g, 4·4 mmol) in a minimum volume of hot water (30 ml) was shaken for 72 h with an excess of diphenylphosphinodithioic acid (5·70 g, 22·8 mmol) in ethanol (30 ml) to give a pale orange precipitate. After washing with water and ethanol, this was recrystallised from hot benzene (or dichloromethane) giving bright orange crystals of the *complex* which were washed with diethyl ether and dried *in vacuo* (2·5 g, 84%), m.p. 298—300° (Found: C, 41·9; H, 2·9; P, 8·8; S, 20·0. $C_{24}H_{20}P_2PtS_4$ requires C, 41·6; H, 2·8; P, 8·9; S, 18·5%).

An alternative method of preparation * is by reaction of platinum(II) acetate[3] and excess diphenylphosphinodithioic acid in warm benzene to give an immediate orange precipitate, purified as above.

The compound is fairly soluble in dichloromethane, chloroform, and hot benzene; sparingly soluble in acetone and ethanol; insoluble in water, ethers, and hexane; $\nu_{max.}$ (Nujol) 745s, 718w, 709s, 685s, 619w, 601m, 567s, 485m, 463w, 454w, 360m, 296s.

Bis(diphenylphosphinodithioato)(triphenylphosphine)-platinum(II).—(a) *Bright yellow form.* $Pt(S_2PPh_2)_2$ (0·10 g, 0·15 mmol) was suspended in benzene (10 ml) and shaken with triphenylphosphine (0·04 g, 0·15 mmol) for *ca.* 20 min to give a lemon-yellow solution. Light petroleum (b.p. 100—120°) was then added to the solution giving a flocculent off-white precipitate which on trituration was rapidly converted into a crystalline bright yellow *product.* This was filtered off, washed with more petroleum (b.p. 60—80°), and dried *in vacuo* at 40° for several hours (0·12 g, 93%), m.p. 122° (Found: C, 53·0; H, 3·8; P, 9·7; S, 13·5. $C_{42}H_{35}P_3PtS_4$ requires C, 52·8; H, 3·7; P, 9·7; S, 13·4%); $\nu_{max.}$ (Nujol) 755sh, 750sh, 742m, 706s, 693sh, 687s, 645m, 628w, 612w, 603w, 571s, 539s, 531s, 512m, 500w, 485w, 475w, 450w, 435w, 350m, 319w, 304w, 270w, 260w.

(b) *Pale yellow form.* A solution of the above product in carbon disulphide was cooled to *ca.* 200 K and on addition of an excess of light petroleum (b.p. 100—120°) a pale yellow *solid* was obtained, washed with cold light petroleum (b.p. 60—80°) and air-dried, m.p. 109—110° (Found: C, 52·6; H, 3·6. $C_{42}H_{35}P_3PtS_4$ requires C, 52·8; H, 3·7%); $\nu_{max.}$ (Nujol) 745s, 706s, 690s, 648s, 621w, 612w, 603w, 570s, 540s, 531s, 512m, 495w, 490sh, 465m, 365sh, 360m, 320w, 305w, 280w; $\nu_{max.}$ (CS_2, pale and bright yellow isomers) 742s, 706s, 690s, 675 (variable), 648s, 623w, 612w, 603w, 570s, 540s, 530s, 512m, 495w, 490w.

Both the bright and pale yellow compounds are soluble in dichloromethane and chloroform; sparingly soluble in carbon disulphide, benzene, and acetone and insoluble in ethanol and xylene.

Bis(diphenylphosphinodithioato)triphenylarsine)platinum(II).—A suspension of $Pt(S_2PPh_2)_2$ (0·22 g, 0·31 mmol) in benzene (15 ml) was treated with an excess of triphenylarsine (0·5 g, 1·60 mmol) and shaken for 1 h. Removal of the solvent under vacuum and treatment of the resulting oil with light petroleum (b.p. 60—80°) gave a bright yellow *precipitate* which was washed carefully with light petroleum to remove free triphenylarsine and then dried *in vacuo* (0·29 g, 91%), m.p. 166° (Found: C, 50·7; H, 3·5. $C_{42}H_{35}AsP_2PtS_4$ requires C, 50·5; H, 3·5%). Attempts to obtain a pale yellow isomer by cooling carbon disulphide or dichloromethane solutions of the above product were unsuccessful; $\nu_{max.}$ (Nujol) 750s, 740s, 706s, 689s, 645s, 628w, 612w, 603w, 571s, 539s, 485w, 475m, 468m, 445w, 440sh, 360sh, 342m, 335m, 330m, 315w, 305m, 275w.

Bis(diphenylphosphinodithioato)triphenylstibineplatinum(II).—As above, shaking $Pt(S_2PPh_2)_2$ (0·22 g, 0·31 mmol) and a large excess of triphenylstibine (2·0 g, 5·7 mmol) in benzene. Solvent removal under vacuum and treatment with dichloromethane and ethanol gave the product as a bright yellow *powder.* Excess of triphenylstibine was removed by repeated washing with light petroleum (b.p. 60—80°) (0·18 g, 55%), m.p. 130—132° (Found: C, 48·2; H, 3·4. $C_{42}H_{35}P_2PtS_4Sb$ requires C, 48·2; H, 3·4%); $\nu_{max.}$ (Nujol) 749w, 730s, 706s, 687s, 643m, 626w, 612w, 603w, 572s, 539s, 483m, 472m, 445m, 365w, 350m, 312w, 305w, 290w, 273s, 265s.

Bis(diphenylphosphinodithioato)(dimethylphenylphosphine)platinum(II).—A suspension of $Pt(S_2PPh_2)_2$ (0·23 g, 0·32 mmol) was shaken in benzene (20 ml) with dimethylphenylphosphine (0·05 ml, 0·30 mmol) under nitrogen for 2 h. After removal of any unreacted $Pt(S_2PPh_2)_2$, solvent was removed under vacuum and the residue treated with light petroleum (b.p. 40—60°) to give a pale yellow *product* (0·26 g, 95%), m.p. 156—158° [Found: C, 46·3; H, 3·7%; *M* (Osmometric in $CHCl_3$), 790 (0·02 g ml^{-1}), 953 (0·11 g ml^{-1}). $C_{32}H_{31}P_3PtS_4$ requires C, 46·2; H, 3·7%; *M*, 831]; $\nu_{max.}$ (Nujol) 745s, 718w, 712s, 709s, 690s, 645m, 623w, 615w, 603w, 571s, 539s, 483s, 471sh, 460w, 443m, 368m, 360m, 325w, 305w, 285w, 265w.

Bis(diphenylphosphinodithioato)(methyldiphenylphosphine)platinum(II).—Method as above, $Pt(S_2PPh_2)_2$ (0·24 g, 0·32 mmol) and methyldiphenylphosphine (0·07 ml, 0·30 mmol) giving a pale yellow product (0·31 g, 98%), m.p. 206—209° [Found: C, 49·9; H, 3·9%; *M* (Osmometric in $CHCl_3$), 767 (0·02 g ml^{-1}), 964 (0·04 g ml^{-1}). $C_{37}H_{33}P_3PtS_4$ requires C, 49·7; H, 3·7%; *M*, 893]; $\nu_{max.}$ (Nujol) 740s, 720m, 709s, 690s, 645m, 621w, 612w, 603w, 571s, 541s, 510s, 488m, 455m, 430w, 365w, 360m, 312w, 305sh, 260w.

(*Diphenylphosphinodithioato*)*bis*(*triphenylphosphine*)-

* Another method of synthesis (from H_2PtCl_6 and Ph_2PS_2H) is also available: A. Muller, V. V. Krishna Rao, and G. Klinsiek, *Chem. Ber.*, 1971, **104**, 1892.

platinum(II) *Diphenylphosphinodithioate*.—$Pt(S_2PPh_2)_2$ (0·11 g, 0·16 mmol) in dichloromethane or benzene (20 ml) on shaking for 15 min with excess triphenylphosphine (0·20 g, 0·75 mmol) gave a colourless solution. Removal of solvent under vacuum gave a semi-crystalline mass which on trituration with light petroleum (b.p. 40—60°) gave an off-white *powder* (0·09 g, 55%), m.p. 69—70° (Found: C, 61·0; H, 4·3; P, 10·4; S, 10·7. $C_{60}H_{50}P_4PtS_4$ requires C, 60·7; H, 4·2; P, 10·4; S, 10·8%).

The compound is soluble in dichloromethane and chloroform; largely dissociated to $[Pt(S_2PPh_2)_2PPh_3]$ in benzene, carbon disulphide, and insoluble in light petroleum; $\nu_{max.}$ (Nujol) 743s, 720w, 710sh, 695s, 655m, 615w, 603w, 573s, 563s, 545s, 528s, 513s, 497s, 487s, 445w, 423w, 361m, 310m, 290w, 275w.

(*Diphenylphosphinodithioato*)*bis*(*dimethylphenylphosphine*)*platinum*(II) *Diphenylphosphinodithioate*.—Method as above, except under nitrogen, $Pt(S_2PPh_2)_2$ (0·23 g, 0·32 mmol) and excess dimethylphenylphosphine (0·12 ml, 0·70 mmol) gave a white *powder*, m.p. 110° [Found: C, 49·5; H, 4·4; P, 11·4; S, 12·8%; *M* (Osmometric in $CHCl_3$), 577 (0·004 g ml^{-1}), 430 (0·009 g ml^{-1}). $C_{40}H_{52}P_4PtS_4$ requires C, 49·5; H, 4·3; P, 12·7; S, 13·2%; *M* (for 1 : 1 electrolyte), 485]; $\nu_{max.}$ (Nujol) 745s, 720m, 710m, 698sh, 690s, 656s, 615w, 603w, 570s, 562s, 495sh, 485s, 470w, 450w, 432m, 365m, 312w, 305w.

(*Diphenylphosphinodithioato*)*bis*(*methyldiphenylphosphine*)*platinum*(II) *Diphenylphosphinodithioate*.—Method as above, $Pt(S_2PPh_2)_2$ (0·18 g, 0·25 mmol) and excess methyldiphenylphosphine (0·20 ml, 0·85 mmol) in dichloromethane giving a white *powder* (0·22 g, 78%), m.p. 62—64° (Found: C, 54·6; H, 3·9. $C_{50}H_{46}P_4PtS_4$ requires C, 54·9; H, 4·2%); $\nu_{max.}$ (Nujol) 740s, 720m, 710m, 690s, 655m, 615w, 603w, 571s, 562s, 521m, 509m, 487m, 450m, 430w, 365m, 310w.

(*Diphenylphosphinodithioato*)*bis*(*dimethylphenylphosphine*)*platinum*(II) *Tetraphenylborate*.—$[Pt(S_2PPh_2)(PMe_2Ph)_2]S_2PPh_2$ (0·10 g, 1·1 mmol) in a minimum volume of acetone (3 ml) was treated with a concentrated aqueous solution of sodium tetraphenylborate (1·0 g, 3·3 mmol). The immediate white precipitate was filtered off, washed thoroughly with distilled water, and then recrystallised from dichloromethane–light petroleum (b.p. 60—80°), m.p. 161—165° (Found: C, 60·5; H, 5·0. $C_{52}H_{52}BP_3PtS_2$ requires C, 60·1; H, 5·0%); $\nu_{max.}$ (Nujol) 790m, 755w, 745s, 740s, 730s, 720s, 709s, 690sh, 685m, 625w, 615w, 603m, 573s, 490m, 480m, 450w, 435w, 370m, 310m, 290w.

(*Diphenylphosphinodithioato*)*bis*(*dimethylphenylphosphine*)*platinum*(II) *Chloride*.—$[Pt(S_2PPh_2)(PMe_2Ph)_2]S_2PPh_2$ was shaken in dichloromethane with an excess of Biorad anion exchange resin (AG-1-X10; 200—400 mesh; Cl^- form) for several hours. Filtration, removal of solvent, and trituration with light petroleum (b.p. 60—80°) gave a white *powder*, m.p. 180—183° (decomp.) (Found: C, 44·2; H, 4·2; Cl, 4·6. $C_{28}H_{32}ClP_3PtS_2$ requires C, 44·5; H, 4·2; Cl, 4·7%); $\nu_{max.}$ (Nujol) 745s, 725s, 715s, 710s, 700s, 690s, 615w, 603w, 573s, 495m, 485m, 460m, 440w, 370m, 310m, 280w.

Bis{1-2-*bis*(*diphenylphosphinoethane*)}*platinum*(II) *Bis*(*diphenylphosphinodithioate*).—$Pt(S_2PPh_2)_2$ (0·20 g, 0·30 mmol) suspended in benzene with an excess of 1-2-bis(diphenylphosphinoethane) (1·0 g, 2·5 mmol) gave an immediate white precipitate, m.p. 245—248° (decomp.) (Found: C, 50·6; H, 4·6. $C_{76}H_{72}P_6PtS_4$ requires C, 61·2; H, 4·6%); $\nu_{max.}$ (Nujol) 743s, 725m, 709sh, 695s, 675w, 650s, 612w, 563s, 530s, 510m, 487m, 480sh, 470w, 450w, 400w, 350m.

Bis{1-2-*bis*(*diphenylphosphinoethane*)}*platinum*(II) *Bis*(*tetraphenylborate*).—$[Pt(diphos)_2](S_2PPh_2)_2$ and an excess of sodium tetraphenylborate were shaken for 24 h in water–acetone. The white residue was washed with water, acetone, and light petroleum (60—80°) and dried *in vacuo*, m.p. 251—253° (decomp.) (Found: C, 73·3; H, 5·6. $C_{100}H_{88}B_2P_4Pt$ requires C, 73·7; H, 5·4%); $\nu_{max.}$ (Nujol) 790s, 765w, 750m, 745m, 738m, 730m, 709s, 690m, 679w, 621w, 612s, 534s, 512m, 485sh, 480s, 440m, 340m.

Palladium Compounds

$Pd(S_2PPh_2)_2$, $[Pd(S_2PPh_2)_2PR_3]$ (PR_3 = PPh_3, PMe_2Ph, $PEtPh_2$, and PEt_3), and $[Pd(S_2PPh_2)(PR_3)_2]S_2PPh_2$ (PR_3 = PMe_2Ph or PEt_3) were prepared as described previously.[2]

Bis(*diphenylphosphinodithioato*)(*methyldiphenylphosphine*)*palladium*(II).—Method as for $[Pt(S_2PPh_2)_2(PMePh_2)]$, $Pd(S_2PPh_2)_2$ (0·18 g, 0·25 mmol) and methyldiphenylphosphine (0·07 ml, 0·30 mmol) giving an orange crystalline *product* (0·18 g, 80%), m.p. 191—193° (Found: C, 55·2; H, 4·2. $C_{37}H_{33}P_3PdS_4$ requires C, 55·2; H, 4·1%); $\nu_{max.}$ (Nujol) identical to platinum complex.

(*Diphenylphosphinodithioato*)*bis*(*methyldiphenylphosphine*)*palladium*(II) *Diphenylphosphinodithioate*.—As for the corresponding platinum compound giving a pale orange *powder*, m.p. 66—69° (Found: C, 59·5; H, 4·5. $C_{50}H_{46}P_4PdS_4$ requires C, 59·7; H, 4·6%); $\nu_{max.}$ (Nujol) identical to platinum complex.

Bis{1-2-*bis*(*diphenylphosphinoethane*)}*palladium*(II) *Bis*(*diphenylphosphinodithioate*).—As for the corresponding platinum compound, giving an immediate white *precipitate*, m.p. 211—212° (Found: C, 65·6; H, 5·6; P, 12·7; S, 8·7. $C_{76}H_{72}P_6PdS_4$ requires C, 65·0; H, 4·9; P, 13·3; S, 9·3%); $\nu_{max.}$ (Nujol) identical to platinum complex.

Summary of X-Ray Structural Data.—(a) $[Pd(S_2PPh_2)_2PPh_3]$ prepared as in reference 2 gave well-formed triclinic needles from a nitromethane–ether mixture.

Crystal Data.—$C_{42}H_{35}P_3PdS_4$, *M*, 867, $a = 9·62$, $b = 18·65$, $c = 22·13$ Å, $\alpha = 90·5$, $\beta = 90·4$, $\gamma = 92·5°$, $D_m = 1·43$, $D_c = 1·45$ g cm^{-3}; $Z = 4$, space group $B\bar{1}$.

816 Independent reflections were obtained from precession data (Cu-K_α radiation), giving about two-thirds of the reciprocal lattice out to a resolution of 1·5 Å. The positions of the palladium, sulphur, and phosphorus atoms were obtained by Patterson and Fourier syntheses, and the phenyl rings, which are only partially resolved, have been idealised and included in further refinement to give the heavy atom framework shown in the Figure. Further data is being collected to refine the structure fully.

(b) The following preliminary report has been provided by Dr. C. A. Beevers and Mr. A. Fraser of the University of Edinburgh.

'A crystal of $[Pd(S_2PPh_2)_2(PEt_3)_2]S_2PPh_2$, prepared as in reference 2 was mounted about its needle axis and *X*-ray photographs taken by the Weissenberg method. From these photographs, the following cell statistics were calculated: $a = 33·42$; $b = 8·74$; $c = 32·02$ Å; $\beta = 121·2°$, $U = 7400$ Å^3, $Z = 8$; space group $C2/c$. 208 *h*0*l* Reflections were measured visually and a structure with a four-co-ordinate palladium atom refined in two dimensions to an *R* factor of 0·20. All attempts to refine the structure on the basis of a six-co-ordinate palladium atom were unsuccessful.'

Nickel Compounds

Bis(diphenylphosphinodithioato)nickel(II) was prepared as described elsewhere;[13] $\nu_{max.}$ (Nujol) 740s, 709s, 685s, 619w, 601w, 573s, 485m, 463w, 454w, 342m.

Bis(diphenylphosphinodithioato)bis(pyridine)nickel(II).—$Ni(S_2PPh_2)_2$ was suspended in chloroform and an excess of dry pyridine added dropwise. Immediate reaction occurred to give a deep yellow-green solution which on standing for several minutes deposited the pale green crystalline *product*. This was filtered, washed well with diethyl ether, and air-dried m.p. 160° (decomp.) (Found: C, 57·4; H, 4·2; N, 3·7. Calc. for $C_{34}H_{30}N_2NiP_2S_4$: C, 57·1; H, 4·2; N, 3·8%); $\nu_{max.}$ (Nujol) 760s, 750s, 745s, 720w, 705s, 700s, 690s, 645w, 632s, 612s, 570s, 488m, 480m, 460m, 450w, 366s, 308w.

We thank Johnson–Matthey Ltd., for a loan of palladium(II) chloride and the S.R.C. for an award (to J. M. C. A.).

[1/1217 *Received, July 15th*, 1971].

[13] W. Kuchen, J. Metten, and A. Jadat, *Chem. Ber.*, 1964, **97**, 2306.

Metal Complexes of Sulphur Ligands. Part III.[1] Reaction of Platinum(II) *NN*-Dialkyldithiocarbamates, *O*-Ethyl Dithiocarbonate (Xanthate), and *OO'*-Diethyl Dithiophosphate with Tertiary Phosphines

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JOURNAL
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THE CHEMICAL SOCIETY

DALTON TRANSACTIONS

1973

Metal Complexes of Sulphur Ligands. Part III.[1] Reaction of Platinum(II) *NN*-Dialkyldithiocarbamates, *O*-Ethyl Dithiocarbonate (Xanthate), and *OO'*-Diethyl Dithiophosphate with Tertiary Phosphines

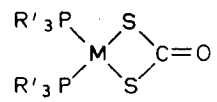
By (Miss) J. M. C. Alison and T. A. Stephenson,* Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ

Evidence is presented to show that the reaction of all $M(S{-}S)_2$ compounds [M = Pt, Pd; $(S{-}S)^- = {}^-S_2CNR_2$ (R = Me, Et), ${}^-S_2COR$ (R = Et, $PhCH_2$), ${}^-S_2P(OEt)_2$, and ${}^-S_2PR_2$ (R = Me, Et, Ph)] with tertiary phosphines occurs by stepwise cleavage of metal–sulphur bonds to generate four-co-ordinate compounds of formulae $[M(S{-}S)_2PR'_3]$ and $[M(S{-}S)(PR'_3)_2](S{-}S)$ with unidentate/bidentate (III) and ionic/bidentate (IV) co-ordintion respectively. All the ionic compounds readily revert to the $[M(S{-}S)_2PR'_3]$ complexes in the presence of non-polar solvents *via* nucleophilic attack by $(S{-}S)^-$ on the metal. In addition, for $(S{-}S)^- = {}^-S_2COR$, ${}^-S_2P(OEt)_2$, nucleophilic attack can also occur on a co-ordinated alkoxy group to give the novel compounds $[(R'_3P)_2MS_2CO]$ (I) and $[(R'_3P)_2MS_2P(O)OEt]$ (II) respectively.

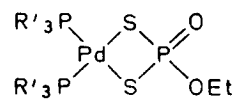
For $[M(S{-}S)(PR'_3)_2](S{-}S)$ compounds containing ${}^-S_2CNR_2$, the presence of excess PR'_3 catalyses the reaction between dithiocarbamate ion and dichloromethane, giving $CH_2(S_2CNR_2)_2$ and $[M(S_2CNR_2)(PR'_3)_2]Cl.H_2O$. These conclusions are based on extensive physico-chemical studies and, in particular, the use of variable temperature ^1H n.m.r. spectroscopy.

RECENTLY, it was reported [2-4] that the reaction of tertiary phosphines with $M(S{-}S)_2$ (1 : 1 molar ratio) [M = Pt, Pd; $(S{-}S)^- = {}^-S_2CNEt_2$, ${}^-S_2COR$, ${}^-S_2P(OEt)_2$, and ${}^-S_2CR$] gave the complexes $[M(S{-}S)_2PR'_3]$ which were formulated as five-co-ordinate compounds on the basis of ^1H n.m.r. data. A brief mention was also made of the precipitation from solution of what may be six-co-ordinate species when an excess of methyldiphenylphosphine was added to platinum(II) compounds of ring-substituted dithiobenzoates [3] but no further details were given. It was also stated [2] that 'diethyldithiocarbamate complexes of palladium(II) and platinum(II) react only slowly (hours) with excess methyldiphenylphosphine to produce what appears to be phosphine co-ordinated substitution products' but a footnote added that 'these reactions have not been characterised completely to date'. When excess tertiary phosphine was added to these xanthate and dithiophosphate adducts, further reaction occurred to give the novel complexes $[(R'_3P)_2MS_2CO]$ (I) and $[(R'_3P)_2PdS_2P(O)OEt]$ (II) respectively,[4] for which no convincing mechanism of formation was suggested.

Other studies, however, on tertiary phosphine complexes of $M(S_2PR_2)_2$ (M = Pd, Pt; R = Ph,[1] Et,[5] Me [5]) and $Pd(S_2PF_2)_2$ [6] have suggested that the 1 : 1 and 1 : 2 adducts formed possess four-co-ordinate square planar structures of type (III) and (IV) respectively and these structural assignments have been confirmed by *X*-ray

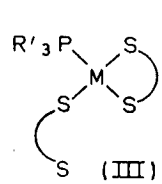


(I)



(II)

analyses on $[Pd(S_2PPh_2)_2PPh_3]$ [7] and $[Pd(S_2PPh_2)(PEt_3)_2]S_2PPh_2$.[8]



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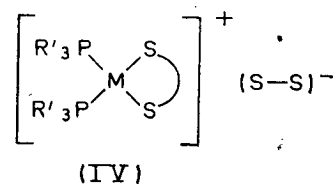


(IV)

In view of these latter results, it was therefore of some interest to re-examine and extend some of the work reported in publications 2—4; the results of this investigation are presented in this paper.

RESULTS AND DISCUSSION

Complexes of Stoicheiometry $[Pt(S_2CNR_2)_2PR'_3]$.—Reaction of $Pt(S_2CNEt_2)_2$ with either PPh_3 or $PMePh_2$ (1 : 1

[1] Part II, (Miss) J. M. C. Alison, T. A. Stephenson, and (in part) R. O. Gould, *J. Chem. Soc.* (*A*), 1971, 3690.
[2] J. P. Fackler, jun., W. C. Seidel, and J. A. Fetchin, *J. Amer. Chem. Soc.*, 1968, **90**, 2707.
[3] J. P. Fackler, jun., J. A. Fetchin, and W. C. Seidel, *J. Amer. Chem. Soc.*, 1969, **91**, 1217.
[4] J. P. Fackler, jun., and W. C. Seidel, *Inorg. Chem.*, 1969, **8**, 1631.
[5] Part IV, D. F. Steele and T. A. Stephenson, to be published.
[6] F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, 1970, **9**, 629.
[7] Miss J. M. C. Alison and R. O. Gould, to be published.
[8] C. A. Beevers and A. Fraser, to be published.

molar ratio) in carbon disulphide gives deep lemon-yellow solutions immediately from which crystalline yellow solids of stoicheiometry $[Pt(S_2CNEt_2)_2PR'_3]$ can be readily isolated. These are non-conducting, diamagnetic, and quite stable both in solid and solution state. For $PR'_3 = PMePh_2$, the ^1H n.m.r. at 301 K is identical to that reported earlier by Fackler *et al.*[2] (Table 1). In a further note,[3] these authors state that 'the p.m.r. behaviour of methyldiphenylphosphinebis-(*NN*-diethyldithiocarbamato)platinum(II) is essentially

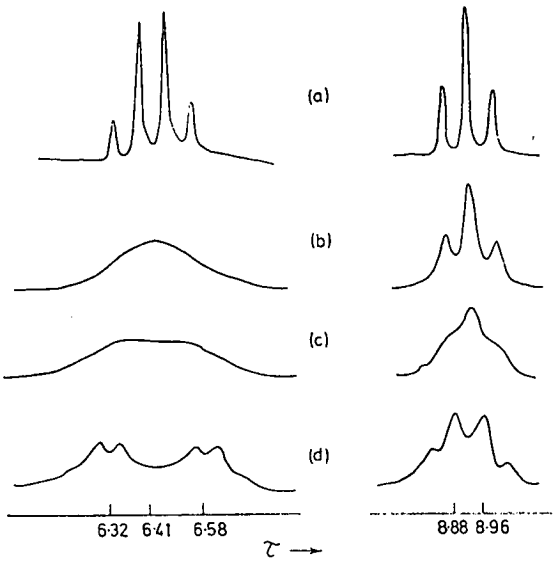


FIGURE 1 Variable temperature ^1H n.m.r. spectrum of $[Pt(S_2CNEt_2)_2PPh_3]$ in $CDCl_3$–CS_2 (for CH_2 quartet and CH_3 triplet) at (a) 301 K, (b) 243 K, (c) 233 K, and (d) 203 K

independent of temperature from room temperature to −70 °C in CS_2'. However, we find that the room-temperature n.m.r. spectrum in $CDCl_3$ or CS_2 is deceptively simple, since on cooling, the CH_2 quartet at τ 6·26 starts to broaden at *ca.* 253 K, coalesces at *ca.* 240 K, and, at 213 K, exhibits a limiting spectrum of two broadened signals (with some unresolved fine structure) centred at τ 6·37 and 6·17 (separation 20 Hz). Likewise, the single CH_3 triplet resonance (τ 8·80) starts to broaden at *ca.* 230 K and, at 213 K consists of an overlapping doublet of triplets centred at τ 8·82 and 8·76 (separation 6 Hz) * (Table 1).

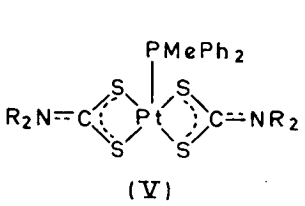
Similarly, $[Pt(S_2CNEt_2)_2PPh_3]$ (Figure 1) exhibits a single CH_2 quartet (τ 6·41) and CH_3 triplet (τ 8·89) at 301 K; at 203 K it has two broadened quartets at τ 6·58 and 6·32 (separation 26 Hz) and an overlapping doublet of triplets at τ 8·96 and 8·88 (separation 8 Hz). A study of the reaction between $Pt(S_2CNMe_2)_2$ and $PMePh_2$ (1 : 1 molar ratios) was also made. Although a pure, solid product could not be isolated by this method, solution studies were consistent with the results discussed above,

* The discrepancy between this behaviour and that reported in ref. 3 may be due to the smaller limiting separation observable on a 60 MHz instrument (3·6 Hz for the CH_3 resonance) in addition to the failure to observe the temperature dependence of the CH_2 quartet in the earlier study.

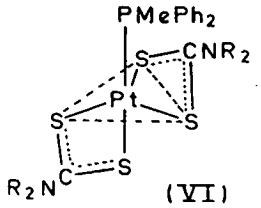
i.e. a single methyl resonance at room temperature, broadening and splitting into two equivalent resonances at lower temperature (Table 1).

All these observations are analogous to those observed for the variable-temperature ^1H n.m.r. spectra exhibited by $[Pt\{S_2P(OEt)_2\}_2PMePh_2]$[3], $[Pt(S_2PMe_2)_2PR'_3]$ (PR'_3 = PPh_3, $PMePh_2$, *etc.*)[5] and the variable-temperature ^{19}F n.m.r. spectrum of $[Pd(S_2PF_2)_2P(MeC_6H_4)_3]$.[6] In all cases, the temperature dependence is completely reversible, indicating that no gross chemical change has occurred. Furthermore, the close similarity of the activation energies for the temperature-dependent reaction manifested by these 1 : 1 adducts of $^-S_2P(OEt)_2$, $^-S_2PMe_2$, and $^-S_2CNR_2$ (estimated from the coalescence temperature by standard methods)[9] (Table 2) is indicative of a common mechanism to produce averaging of the protons attached to the dithioacid ligands. This strongly suggests that for $(S{-}S)^- = {}^-S_2CNR_2$, the observed temperature dependence is *not* due to restricted rotation about the C–N bond as found, for example, in dithiocarbamate esters[10] (Table 2). A full line-shape analysis for all compounds of type $[M(S{-}S)_2(ER'_3)]$ (E = P, As, Sb) is at present in progress to ascertain accurate rate data and will be published later.

The observation of magnetically inequivalent alkyl groups at low temperature for $[Pt(S_2CNR_2)_2PR'_3]$ is inconsistent with the square pyramidal structure (V)

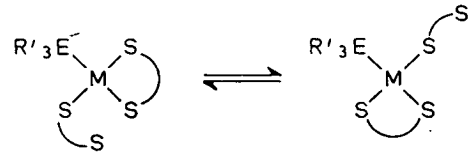


(V)



(VI)

postulated earlier for the low-temperature form,[3] since the alkyl groups in (V) will be magnetically equivalent, even allowing for restricted rotation about the C–N bond. Although the low-temperature spectrum is not incompatible with the five-co-ordinate trigonal-bipyramidal structure (VI), we suggest that a better explanation for the temperature-dependent n.m.r. spectra of *all* the compounds of formula $[M(S{-}S)_2(ER'_3)]$ is the presence of an equilibrium of type (1) between two n.m.r. *equivalent* four-co-ordinate complexes. At higher temperatures, rapid interchange of bidentate and unidentate



(1)

dithio-ligands produces an averaging of the magnetic nuclei attached to the dithio-ligands whereas at lower temperatures, intramolecular rearrangement becomes

[9] J. A. Pople, W. G. Schneider, and H. J. Bernstein, in 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959, p. 223.

[10] C. E. Holloway and M. H. Gitlitz, *Canad. J. Chem.*, 1967, **45**, 2659.

TABLE 1

^{1}H N.m.r. data for various sulphur compounds

Compound	Solvent	T/K	τ Value [a] Dithio-ligand CH_3 [f]	Dithio-ligand CH_2 [g]	$CH_3(PR'_3)$ [b]	Others [c]	J_{PH} [d]	J_{PtH} [e]
$Ph_3(PhCH_2)PS_2CNEt_2$	$CDCl_3$	301	8·86(3) [h]	5·86 (2)		Ph, 2·0—3·0(10) CH_2, 4·58(1) (d) J_{CH_2-P} 14·0 [d]		
$Pt(S_2CNEt_2)_2$	$CDCl_3$	301	8·70(3)	6·40(2)				
$Pt(S_2CNEt_2)_2PPh_3$	$CDCl_3$–CS_2	301	8·89(12)	6·41(8)		Ph, 2·2—2·8(15)		
		203	8·96(6); 8·88(4)	6·58(4); 6·32(4)				
$Pt(S_2CNEt_2)_2(PMePh_2)$	$CDCl_3$	301	8·80(12)	6·26(8)			10·0	38·0
					7·72(3)	Ph, 2·2—2·6(10)		
		213	8·82(6); 8·76(6)	6·37(4); 6·17(4)				
$[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$	$CDCl_3$	301	8·80(6)	6·26[4] [i] 6·09	8·16(3) (s) (br)			
						Ph, 2·4—2·6(10)		
		213	8·80(6)	—6·37(2); 5·77(2)	8·09(3)		9·0 [j]	34·0
$Pt(S_2CNMe_2)_2(PMePh_2)$	$CDCl_3$–CS_2	301	6·64(12) (s)				10·7	35·0
					7·69(3)	Ph, 2·6(10)		
		193	6·81(6) (s); 6·46(6) (s)					
$[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$	$CDCl_3$	301	6·71 (s) [6] [i] 6·53 (s)		8·30(3) (s)			
						Ph, 2·6(10)		
		213	—6·65(3) (s); 6·39(3) (s)		8·10(3)		9·5 [j]	35·0
$[Pt(S_2CNEt_2)(PPh_3)_2]Cl,H_2O$	$CDCl_3$	301	8·78(3)	6·40(2)		Ph, 2·6(15) H_2O, 7·8(1) [k]		
$[Pt(S_2CNEt_2)(PPh_3)_2]PF_6$	$CDCl_3$	301	8·75(3)	6·42(2)		Ph, 2·6(15)		
$[Pt(S_2CNEt_2)(PPh_3)_2]BPh_4$	$CDCl_3$	301	8·94(3)	6·68(2)		Ph, 2·5—3·2(25)		
$[Pt(S_2CNEt_2)(PMePh_2)_2]Cl,H_2O$	$CDCl_3$	301	8·73(3)	6·36(2)	8·06(3)	Ph, 2·6(10) H_2O, 7·20(1) [k]	10·0 [j]	34·0
		253	8·73(3)	6·36(2)	8·06(3)	H_2O, 7·00(1) [k]		
$[Pt(S_2CNEt_2)(PMePh_2)_2]PF_6$	$CDCl_3$	301	8·72(3)	6·38(2)	8·06(3)	Ph, 2·5(10)	10·0 [j]	35·0
$[Pt(S_2CNEt_2)(PMePh_2)_2]BPh_4$	$CDCl_3$	301	8·84(3)	6·56(2)	8·30(3)	Ph, 2·5—3·2(20)	10·0 [j]	35·0
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]Cl,H_2O$	$CDCl_3$	301	8·62(3)	6·22(2)	8·20(6)	Ph, 2·6(5), H_2O, 8·10(1) [k]	10·0 [j]	35·0
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]BPh_4$	$CDCl_3$	301	8·74(3)	6·40(2)	8·60(6)	Ph, 2·5—3·2(15)	10·0 [j]	34·0
$[Pt(S_2CNMe_2)(PPh_3)_2]Cl,H_2O$	$CDCl_3$	301	6·70(3) (s)			Ph, 2·6—2·7(15) H_2O, 7·9(1) [k]		
$[Pt(S_2CNMe_2)(PPh_3)_2]BPh_4$	$CDCl_3$	301	7·40(3) (s)			Ph, 2·6—3·2(25)		
$[Pt(S_2CNMe_2)(PMePh_2)_2]Cl,H_2O$	$CDCl_3$	301	6·73(3) (s)		8·10(3)	H_2O, 7·50(1) [k]	10·0 [j]	36·0
		243	6·73(3) (s)		8·10(3)	Ph, 2·6(10) H_2O, 7·10(1) [k]		
$[Pt(S_2CNMe_2)(PMePh_2)_2]BPh_4$	$CDCl_3$	301	7·25(3) (s)		8·35(3)	Ph, 2·6—3·2(25)	10·0 [j]	35·0
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]Cl,2H_2O$	$CDCl_3$	301	6·55(3) (s)		8·10(6)	Ph, 2·5(5); H_2O, 7·70(2) [k]	10·0 [j]	35·0
$[Pd(S_2CNMe_2)(PMe_2Ph)_2]Cl,2H_2O$	$CDCl_3$	301	6·60(3) (s)		8·35(6) (s)	Ph, 2·6(5); H_2O, 7·80(2) [k]		
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]BPh_4$	$CDCl_3$	301	7·05(3) (s)		8·65(6)	Ph, 2·6—3·2(15)	10·0 [j]	37·0
$CH_2(S_2CNEt_2)_2$	$CDCl_3$	301	8·83(6)	6·28(2); 5·96(2)		CH_2, 4·60(1) (s)		
		313	8·83(6)	6·12(4) (s)				
$CH_2(S_2CNMe_2)_2$	$CDCl_3$	301	6·66(3) (s); 6·45(3) (s)			CH_2, 4·64(1) (s)		
		313	6·57(6) (s)					
$[Pt_2\{S_2P(OEt)_2\}_2PPh_3]$	$CDCl_3$	301	8·70(12)	5·90(8) [l]		Ph, 2·6(15)		
		213	8·74(6); 8·66(6)	5·90(8) [l]				
$[Pt\{S_2(OEt)_2AsPh_3\}]$ [m]	$CDCl_3$	301	8·69(12)	6·00(8) [l]		Ph [n]		
		223	8·71(6); 8·62(6)	6·00(8) [l]				
$[Pt\{S_2P(OEt)_2(PPh_3)\}_2]BPh_4$	$CDCl_3$	301	8·66(3)	5·88(2) [o]		Ph, 2·5—3·2(25)		
$Pt(S_2P(O)OEt)(PPh_3)_2$	$CDCl_3$	301	8·80(3)	6·05(2) [o]		Ph, 2·5—2·8(30)		
$Pt(S_2COEt)_2PPh_3$	$CDCl_3$	301	8·62(6)	5·46(4)		Ph, 2·5(15)		
	CS_2	183	8·62(6) (s) (br)	5·46(4) (s) (br)				
$[Pt(S_2COEt)(PPh_3)_2]BPh_4$	$CDCl_3$	301	8·66(3)	5·58(2)		Ph, 2·5—3·2(50)		

s(singlet); d(doublet); br(broad).

[a] ±0·01. [b] Triplet of doublets unless otherwise stated. [c] Phenyl resonance; complex multiplet. [d] ±0·2 Hz. [e] ±0·5 Hz. [f] Triplet unless otherwise stated ($J_{CH_2CH_3}$ 7·0 Hz). [g] Quartet unless otherwise stated ($J_{CH_2CH_3}$ 7·0 Hz). [h] Numbers in parentheses indicate normalised integrated intensities. [i] Two resonances of total intensity [ ] [j] Since $H_nPP'H_n'$ type spectrum, coupling constant is $|J_{PH} + J_{PH'}|$. [k] τ Value is concentration dependent. [l] Complex multiplet. [m] $Pt\{S_2P(OEt)_2\}_2$ + excess $AsPh_3$ *in situ*. [n] Not recorded since an excess of $AsPh_3$ present. [o] Overlapping doublet of quartets with $J_{CH_2CH_3}$ 7·0 Hz; J_{CH_3-P} 9·4 Hz.

sufficiently slow for the 'frozen-out' n.m.r. spectrum to be observed.*

It should be noted that for $(S-S)^- = {}^-S_2CNR_2$, the limiting low-temperature spectra are not *completely* consistent with those expected for the frozen-out structure (VII). Even assuming that rotation about the Pt–S and C–N bonds of the unidentate dithio-group is sufficiently rapid to average R^1 and R^2, R^3 and R^4 are magnetically inequivalent and three resonances of intensity ratio 1 : 1 : 2 are theoretically expected, whereas only two resonances are observed.

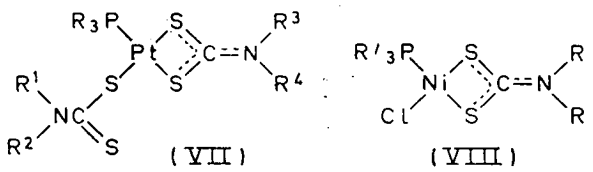
TABLE 2

Free-energy of activation and coalescence temperature (T_c/K) obtained from ^{1}H n.m.r. spectra for various sulphur compounds

Compound	T_c/K [a]	$\Delta G^*_{T_c}$ [b]
$Pt\{S_2P(OEt)_2\}_2PPh_3$	238 [c]	52·3
$Pt(S_2PMe_2)_2PPh_3$	263	55·5
$Pt(S_2CNEt_2)_2PPh_3$	243 [d]	50·8
	233 [e]	51·2
$Pt(S_2CNEt_2)_2PMePh_2$	238 [d]	50·2
	228 [e]	49·6
$Pt(S_2CNMe_2)_2PMePh_2$	213	43·8
$[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$	253 [d]	51·2
$[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$	223	46·5
$CH_2(S_2CNEt_2)_2$	233	65·7 [e]
$CH_2(S_2CNMe_2)_2$	243	64·4 [f]

[a] ±1 K. [b] ±1·0 kJ mol^{-1}. [c] Measured on CH_3 triplets. [d] Measured on CH_2 quartets. [e] *Cf.* $EtSCSNEt_2$[10] $\Delta G^*_{298\ K}$ 63·8 kJ mol^{-1}. [f] *Cf.* $MeSCSNMe_2$[10] $\Delta G^*_{298\ K}$ 61·8 kJ mol^{-1}.

However, the atoms (S and P) inducing the magnetic inequivalence in R^3 and R^4 are well removed (six bonds) from these groups, so that the separation between the R^3 and R^4 resonances may well be too small to be resolved, particularly at 213 K where machine line-broadening is also appreciable. A similar inconsistency is found for the square-planar compounds $[Ni(S_2CNR_2)Cl(PR'_3)]$ [12]



(VII) (VIII)

(VIII) (*one* R resonance at 213 K) [13] and even in compounds such as $Me_2NCOS(SiH_3)$ where the magnetic inequivalence is produced by atoms (S and O), four bonds removed from the methyl protons, the separation at 301 K of the two methyl groups is only 12 Hz.[14]

* A similar conclusion has recently been reached by Powell and Chan[11a] for these compounds on the basis of detailed variable-temperature ^{1}H n.m.r. studies on the related complexes [π-allyl $Pd(PMe_2Ph)(X-Y)$] (X–Y = $^-S_2CNMe_2$, $^-S_2COMe$). In addition Davis *et al.*[11b] invoke a similar mechanism for interconversion processes in molybdenum dialkyldithiocarbamates.

† As pointed out by a referee, we have assumed that the *essential* feature of the solid-state structure (*viz.* the unidentate–bidentate co-ordination) is retained in solution, but this assumption is strongly supported by both the characteristic chemical shifts of the two CH_2 quartets for the dithiocarbamate compounds and by the characteristic i.r. bands for the dithiophosphinate compounds.

‡ *Note added in proof:* An *X*-ray structural analysis of $[Pt(S_2CNEt_2)_2PMePh_2]$ by J. M. C. Alison and R. O. Gould is now sufficiently advanced to show unequivocally that the structure in the solid state is also of type III.

Although we are unable to rule out unequivocally the presence of a five-co-ordinate trigonal bipyramidal structure to explain the low-temperature ^{1}H n.m.r. data, there is a substantial amount of evidence which supports the interpretation given in equation (1). This is as follows. (i) There is a very close similarity of chemical shifts and coupling constants (for the methyl phosphine ^{1}H n.m.r. resonance at 301 K) for *all* the dithio-compounds $[Pt(S-S)_2(PMePh_2)]$,[1,2,5] which is indicative of a similar structure and the *X*-ray analysis of $[Pd(S_2PPh_2)_2PPh_3]$ [7] (isomorphous with the corresponding platinum complex) shows this to be of type (III).†‡ Furthermore, for $[Pt(S_2CNEt_2)_2PMePh_2]$, the position of the low-field CH_2 quartet (τ 6·17) is intermediate between those found for ionic [τ 5·86 in $Ph_3(PhCH_2)PS_2CNEt_2$] and bidentate [τ 6·40 in $Pt(S_2CNEt_2)_2$] diethyldithiocarbamate groups, suggesting that it probably arises from a unidentate group.

(ii) For the $^-S_2PPh_2$ compounds reported earlier,[1] both room- and low-temperature isomeric forms of $[M(S_2PPh_2)_2PPh_3]$ (M = Pt, Pd) can be isolated. However, the characteristic i.r. bands of 'bidentate' and 'unidentate' dithiophosphinate co-ordination [1] remain unchanged which suggests that a structure of type (III) persists at all temperatures.

(iii) Reaction of either $Pt(S-S)_2$ or $[Pt(S-S)_2PR'_3]$ with an excess of tertiary phosphine gives ionic species containing the $[Pt(S-S)(PR'_3)_2]^+$ cation (see later) which is indicative of stepwise cleavage of metal–sulphur bonds by tertiary phosphine.

Therefore, all this evidence suggests (to us) that a structure of type (III) is more feasible than a five-co-ordinate formulation; however, as in all interpretations, utilising 'sporting' methods, a degree of uncertainty naturally remains.

Platinum(II) NN-*Dialkyldithiocarbamates with an Excess of Tertiary Phosphine.*—If a suspension of $Pt(S_2CNEt_2)_2$ in acetone is treated with an excess of $PMePh_2$, a pale yellow solution is formed from which pale yellow crystals are rapidly deposited. This compound has an analysis consistent with the formula $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$; the ionic formulation is confirmed by the presence of additional i.r. bands corresponding to those found in $NaS_2CNEt_2,3H_2O$ (but not in co-ordinated dithiocarbamate groups) and the ready synthesis of $[Pt(S_2CNEt_2)(PMePh_2)_2]BPh_4$. As noted earlier [1] for the ionic PR'_3 complexes of $Pt(S_2PPh_2)_2$, this complex also readily dissociates to $[Pt(S_2CNEt_2)_2(PMePh_2)]$ in the presence of nonpolar solvents. In this instance, the increased nucleophilicity of $^-S_2CNEt_2$ compared to $^-S_2PPh_2$ [15] enhances this tendency. Thus, although the

[11] (*a*) J. Powell and A. W. L. Chan, *J. Organometallic Chem.*, 1972, **35**, 203; (*b*) R. Davis, M. N. S. Hill, C. E. Holloway, B. F. G. Johnson, and K. H. Al-Obaidi, *J. Chem. Soc.* (*A*), 1971, 994.

[12] P. L. Maxfield, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 693.

[13] J. A. McCleverty, personal communication.

[14] C. Glidewell and D. W. H. Rankin, *J. Chem. Soc.* (*A*), 1970, 279.

[15] P. Porta, A. Sgamellotti, and N. Vinciguerra, *Inorg. Chem.*, 1968, **7**, 2625.

ionic complex is insoluble in benzene, a yellow solution slowly forms with time and $[Pt(S_2CNEt_2)_2(PMePh_2)]$ is isolated. Even in diethyl ether, a suspension of the ionic complex turns deep yellow (24 h) and the neutral compound is recovered.

The ^1H n.m.r. spectrum of the ionic compound in $CDCl_3$ is of some interest (Figure 2). At room temperature, a deep yellow solution is formed and although the integration of $^-S_2CNEt_2$ to $PMePh_2$ protons is correct for $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$, the equilibrium lies well to the right-hand side of equation (2). This is evident since the position of the CH_2 quartet (τ 6·26)

$$[Pt(S_2CNR_2)(PMePh_2)_2]S_2CNR_2 \rightleftharpoons [Pt(S_2CNR_2)_2PMePh_2] + PMePh_2 \quad (2)$$

is identical to that found for $[Pt(S_2CNEt_2)_2PMePh_2]$ at room temperature and since there is a further quartet

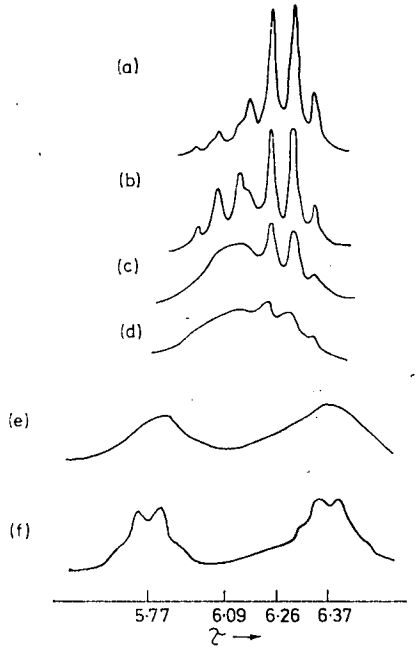


FIGURE 2 Variable-temperature ^1H n.m.r. spectrum of $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ in $CDCl_3$ (CH_2 quartet) at (a) 301 K, (b) 283 K, (c) 263 K, (d) 256 K, (e) 223 K, and (f) 213 K

of lower intensity centred at τ 6·09, which we attribute to the ionic complex. In addition, the methyl phosphine resonance is a broad singlet at τ 8·16 {*cf.* for $[Pt(S_2CNEt_2)_2PMePh_2]$, a triplet of doublets centred at τ 7·72},[2] indicative of rapid exchange between free and bound phosphine.

However, on cooling, the solution becomes progressively paler and the ^1H n.m.r. shows the growth of the quartet at τ 6·09, accompanied by a decrease in intensity of the quartet at τ 6·26. At 273 K, the two quartets are of comparable intensity but at 263 K, the low-field quartet starts to broaden, whilst the one at high-field remains sharp. At 253 K, a single broad resonance is observed and further lowering of temperature to 213 K produces two quartets at τ 6·37 (bidentate) and 5·77 (ionic) (separation 60 Hz). In addition, the methyl phosphine resonance sharpens such that at 213 K, a strong doublet, centred at τ 8·09 with weak ^{195}Pt satellites is observed {*cf.* $[Pt(S_2PPh_2)(PMePh_2)_2]S_2PPh_2$ [1] with a triplet of doublets at τ 7·99}. Raising of the temperature to 301 K shows the process is reversible, the pale yellow solution once more becoming deep yellow.

Thus, down to *ca.* 265 K, the ^1H n.m.r. changes signify a shift to the left-hand side of equation (2). A similar observation was made earlier [16] for $[Pd(S_2PPh_2)(PEt_3)_2]S_2PPh_2$ where the intensity of the 560 cm^{-1} i.r. band (characteristic of a 1 : 2 compound) increased with respect to the 540 cm^{-1} band (characteristic of a 1 : 1 compound) as the temperature was lowered. In this instance, an estimate of the equilibrium constant for (2) can be computed from the ^1H n.m.r. data. This gives $K_{300\ K}$ 0·33 mol l^{-1}, ΔH 60 kJ mol^{-1}, ΔS 191 J K^{-1} mol^{-1}. Below 265 K, the ^1H n.m.r. changes are interpreted as a slowing down of the exchange between ionic and bidentate dithiocarbamate groups such that at 213 K, the spectrum corresponds to that expected for a 'frozen-out' ionic structure of type (IV) [{*cf.* $[Pd(S_2PF_2)(PPh_3)_2]S_2PF_2$[6]}. The absence at 213 K of a quartet at τ 6·17 shows that the equilibrium lies completely to the left-hand side of (2) at this temperature. From the coalescence temperature (*ca.* 250 K), an estimate of the activation energy for the interchange of ionic and bidentate groups can be obtained (Table 2).

Similarly, reaction of $Pt(S_2CNMe_2)_2$ and an excess of $PMePh_2$ in acetone gives a crystalline sample of $[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$. Detailed ^1H n.m.r. studies in $CDCl_3$ show the same phenomenon as above, namely, a methyl ($^-S_2CNMe_2$) resonance (τ 6·71) at 301 K, corresponding to $[Pt(S_2CNMe_2)_2(PMePh_2)]$ and when the temperature is lowered, the growth of a peak at τ 6·53 (1 : 2 complex), followed by broadening (*ca.* 220 K) and splitting into two equivalent resonances at τ 6·65 and 6·39 (213 K). Analysis of the higher-temperature region gives $K_{300\ K}$ 0·22 mol l^{-1}, ΔH 69 kJ mol^{-1}, ΔS 218 JK^{-1} mol^{-1} and, from the coalescence temperature, an estimate of the activation energy for ionic–bidentate ligand exchange can be obtained (Table 2). All attempts to synthesise $[Pt(S_2CNEt_2)(PPh_3)_2]S_2CNEt_2$ have been unsuccessful, the only product isolated being $[Pt(S_2CNEt_2)_2PPh_3]$ [*cf.* the $Pd(S_2PPh_2)_2$–PPh_3 system].[1,16]

If the reactions between $Pt(S_2CNEt_2)_2$ and an excess of PR'_3 are carried out in dichloromethane solution, the initial pale yellow solutions slowly decolourise during several hours, the qualitative rate of decolouration being $PMe_2Ph \simeq PMePh_2 > PPh_3$. This phenomenon is accompanied by a steady rise in conductivity, the value finally corresponding to that expected for a 1 : 1 electrolyte. Concentration of the solution and addition of diethyl ether gives white microcrystalline solids (A). The ^1H n.m.r. of these compounds are similar to those expected for $[Pt(S_2CNR_2)(PR'_3)_2]S_2CNR_2$ (with averaging of ionic and bidentate dithiocarbamate groups) (Table 1)

[16] T. A. Stephenson and B. D. Faithful, *J. Chem. Soc.* (*A*), 1970, 1504.

except that integration of all these compounds shows that there are insufficient dithiocarbamate protons for this formulation. In fact, the ^1H n.m.r. spectra are consistent with the formulation $[Pt(S_2CNEt_2)(PR'_3)_2]X$ (where X is an anion *not* containing protons), except for the presence of an additional weak resonance in the region τ 6—8. The position of this resonance depends on solvent, solute concentration, and temperature; lowering the temperature or increasing the concentration or the solvent polarity shifts the peak to lower field, phenomena indicative of the presence of a hydrogen-bonded species. The dithiocarbamate ethyl resonance is temperature independent and has a chemical shift compatible with bidentate co-ordination. We suggest that the species arising from prolonged reaction of $Pt(S_2CNEt_2)_2$ and an excess of PR'_3 in dichloromethane are the compounds $[Pt(S_2CNEt_2)(PR'_3)_2]Cl{\cdot}H_2O$ (A); we have amassed considerable evidence to support this rather surprising conclusion.

The solid (A) reacts with $NaBPh_4$ or NH_4PF_6 in acetone–methanol solution to give the compounds $[Pt(S_2CNEt_2)(PR'_3)_2]Y$ ($Y = BPh_4^-$, PF_6^-) which have been fully characterised by ^1H n.m.r., analyses, and conductivity measurements (Tables 1, 4, and 3 respectively). An interesting feature of the ^1H n.m.r. of these compounds is the upfield shift (*ca.* 0·2 p.p.m.) of both $^-S_2CNEt_2$ and PR'_3 resonances in the BPh_4^-, compared to the PF_6^- and Cl^- compounds. Similar observations have been made for the $[Pt(S_2PMe_2)(PR'_3)_2]Y$ series [5] and we suggest that this is a consequence of a ring-current effect in the BPh_4^- complex which is, of course, absent in the other compounds. Evidence for a water molecule is based on the appearance of very weak OH stretches and bends in the mull i.r. spectra of compounds (A), the presence of oxygen (established by direct analysis and ESCA measurements *), and the similarity of the position of the hydrogen-bonded resonance to that recently reported for $[Co(CO)_2(PPh_3)_2(H_2O)Cl]$ (τ 7·4).[17] We suggest that the water molecule is hydrogen-bonded to the cation since addition of chloride ion produces no change in its resonance position. The presence of chloride ion is confirmed by direct analysis, ESCA * measurements, and the fact that after treating (A) with a chloride anion-exchange resin for several days, the ^1H n.m.r., i.r. spectra, and m.p. are unchanged.

The chloride ion can only arise, of course, from the dichloromethane used in this reaction. A careful examination of the ethereal filtrate results in the isolation of an organothio-compound, shown by elemental analysis, mass, and ^1H n.m.r. spectroscopy to be $CH_2(S_2CNEt_2)_2$ (B). This compound has been recently prepared in high yield by refluxing sodium diethyldithiocarbamate with anhydrous dichloromethane.[18] We find that, unless both solvent and sodium salt are scrupulously dried, only very small amounts of (B) can be isolated. However, a more convenient method of preparation is by shaking a mixture of $NaS_2CNEt_2 3H_2O$, CH_2Cl_2 (solvent grade), and any tertiary phosphine for 12 h. The reason why the addition of PR'_3 facilitates the formation of (B) is not at present clear. The ^1H n.m.r. spectrum of (B) is of interest in that at room temperature there are two CH_2 quartets. At a higher temperature these coalesce and the estimated free energy of activation for the barrier to free rotation about the C–N bond compares favourably with the value obtained earlier [10] for $EtSCSNEt_2$ (Table 2). Rather surprisingly, this temperature dependence of (B) was not noted in the original preparation.[18]

TABLE 3

Equivalent conductivities (298 K) in CH_2Cl_2 of some platinum dithio-compounds containing tertiary phosphines

Compound	Conc. (10^{-4}M)	Λ [a]
Ph_4AsCl,HCl	9·8	55·3
Bu_4NClO_4	10·1	22·7
	3·1	32·1
$Pt(S_2CNMe_2)_2$	9·2	3·0
$Pt(S_2CNEt_2)_2$	9·4	0·2
$Pt(S_2CNEt_2)_2PPh_3$	16·5	0·7
$Pt(S_2CNEt_2)_2PMePh_2$	17·3	4·3
$[Pt(S_2CNMe_2)(PPh_3)_2]Cl,H_2O$	12·5	34·2
$[Pt(S_2CNMe_2)(PPh_3)_2]BPh_4$	9·0	40·9
$[Pt(S_2CNMe_2)(PMePh_2)_2]Cl,H_2O$	11·2	36·6
$[Pt(S_2CNMe_2)(PMePh_2)_2]BPh_4$	2·4	50·1
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]Cl,2H_2O$	14·7	38·6
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]BPh_4$	8·8	43·8
$[Pt(S_2CNMe_2)(PEtPh_2)_2]BPh_4$	0·4	36·4
$[Pt(S_2CNEt_2)(PPh_3)_2]Cl,H_2O$	6·9	57·5
$[Pt(S_2CNEt_2)(PPh_3)_2]BPh_4$	2·5	51·6
$[Pt(S_2CNEt_2)(PMePh_2)_2]Cl,H_2O$	6·4	57·5
$[Pt(S_2CNEt_2)(PMePh_2)_2]BPh_4$	10·2	42·2
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]Cl,H_2O$	7·9	50·1
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]BPh_4$	5·9	42·7
$[Pt\{S_2P(OEt)_2\}(PPh_3)_2]BPh_4$	9·4	27·7
$[Pt(S_2COEt)(PPh_3)_2]BPh_4$	10·2	21·6
$Pt(S_2P\{OEt\}_2)_2$ + excess PPh_3	10·0	31·0

[a] In Ω^{-1} cm^2 mol^{-1}.

The mechanism of formation of (A) is most likely *via* prior formation of $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$. Support for this hypothesis comes from a study of the behaviour of $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ in CH_2Cl_2. The initial deep yellow solution, containing a mixture of 1 : 2, 1 : 1 compounds, and free $PMePh_2$, slowly decolourises, a change accompanied by a steady rise in conductivity (Table 5). Removal of the solvent and addition of diethyl ether gives a precipitate of $[Pt(S_2CNEt_2)(PMePh_2)_2]ClH_2O$ and the ethereal filtrate contains $CH_2(S_2CNEt_2)_2$. Similarly, in $CHCl_3$ (plus ethanol stabiliser) the solution also decolourises and (A) is formed. In this instance, the nature of the organic side-products has not been investigated. This is to be contrasted with the behaviour of $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ in ethanol-free $CHCl_3$ and $CDCl_3$ (see earlier), where only nucleophilic attack of $^-S_2CNEt_2$ on the platinum ion occurs. At this juncture, it is not obvious (to us) why ethanol has such a profound effect on the course of the reaction.

* We thank Dr. M. Barber and Mr. P. Swift of A.E.I. Scientific Apparatus Ltd. for these measurements.

[17] J. A. Bowden and R. Colton, *Austral. J. Chem.*, 1968, **21**, 891.

[18] P. R. Heckley, D. G. Holah, A. N. Hughes, and F. Leh, *Canad. J. Chem.*, 1970, **48**, 3827.

Finally, prolonged reaction of $Pt(S_2CNMe_2)_2$ and an excess of PR'_3 in CH_2Cl_2, followed by precipitation with diethyl ether gives a mixture of $[Pt(S_2CNMe_2)(PR'_3)_2]Cl,H_2O$ and $CH_2(S_2CNMe_2)_2$. The latter, which can be extracted with benzene, is best prepared by shaking a mixture of NaS_2CNMe_2, CH_2Cl_2, and a tertiary phosphine (PPh_3, $PMePh_2$, and PMe_2Ph were successfully used). Without the phosphine, the only product is tetramethylthiuram disulphide. Again, the room-temperature ^1H n.m.r. shows two CH_3 resonances, which coalesce at a higher temperature (Table 2). Similarly $Pd(S_2CNMe_2)_2$ and an excess of PMe_2Ph in CH_2Cl_2 give $[Pd(S_2CNMe_2)(PMe_2Ph)_2]Cl2H_2O$.

^1H N.m.r. for all these compounds are given in Table 1, conductivities in Tables 3 and 5, and some analyses in Table 4.

TABLE 4

Analytical data for some platinum(II) dithio-compounds

Compound	M.p. (°C)	Found (%) C	H	N	Others	Required (%) C	H	N	Others
$Pt(S_2CNEt_2)_2PPh_3$	150—152	44·9	4·6	4·0		44·6	4·6	3·7	
$Pt(S_2CNEt_2)_2PMePh_2$	163—165	40·2	4·7	4·4		39·9	4·8	4·1	
$[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$	135—138	44·6	4·3	3·4		46·0	4·6	3·3	
$[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$	132—133	48·5	5·2	3·5	S, 14·2	48·5	5·2	3·2	S, 14·4
$[Pt(S_2CNMe_2)(PPh_3)_2]Cl,H_2O$	196—197	51·8	4·2	2·4		52·4	4·3	1·6	
$[Pt(S_2CNMe_2)(PPh_3)_2]BPh_4$	223—226	65·7	4·9	1·3		65·3	4·8	1·2	
$[Pt(S_2CNMe_2)(PMePh_2)_2]Cl,H_2O$	120—124	45·3	4·3	2·3	Cl, 4·4	45·3	4·4	1·8	Cl, 4·6
$[Pt(S_2CNMe_2)(PMePh_2)_2]BPh_4$	198—203	61·5	5·0	1·5		61·5	5·0	1·4	
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]Cl,2H_2O$	109—111	34·7	4·6	2·5	Cl, 5·7	35·4	4·6	2·2	Cl, 5·5
$[Pt(S_2CNMe_2)(PMe_2Ph)_2]BPh_4$	144—148	57·3	5·3	1·9		56·7	5·3	1·5	
$[Pt(S_2CNEt_2)(PPh_3)_2]Cl,H_2O$	174—175	53·1	4·4	1·7		53·4	4·6	1·5	
$[Pt(S_2CNEt_2)(PPh_3)_2]BPh_4$	94—97	66·2	5·1	1·4		65·8	5·1	1·2	
$[Pt(S_2CNEt_2)(PMePh_2)_2]Cl,H_2O$	210—212	47·6	4·5	1·6	Cl, 4·5 [a]	46·8	4·5	1·8	Cl, 4·5 [a]
$[Pt(S_2CNEt_2)(PMePh_2)_2]BPh_4$	169—171	62·4	5·2	1·3		62·2	5·3	1·3	
$[Pt(S_2CNEt_2)(PMe_2Ph)_2]Cl,H_2O$	99—100	38·9	5·2	2·2	Cl, 5·3	37·5	5·1	2·1	Cl, 5·3
$Pt\{S_2P(OEt)_2\}_2PPh_3$	97—101	38·1	4·2			37·7	4·2		
$Pt(S_2P(O)OEt)(PPh_3)_2$	227—230	51·2	4·0			52·1	4·0		
$[Pt\{S_2P(OEt)_2\}(PPh_3)_2]BPh_4$	84—86	61·9	4·8			62·1	5·0		
$Pt(S_2COEt)_2PPh_3$	164—169	42·5	3·4			41·4	3·6		
$[Pt(S_2COEt)(PPh_3)_2]BPh_4$	86—90	65·4	5·0			65·2	4·8		

[a] Found, O, 1·1. Required, 2·0%.

TABLE 5

Variation of equivalent conductivity with time for some platinum(II) dithio-compounds

$[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$ ($7{\cdot}1{\cdot}10^{-4}$M) in CH_2Cl_2

Time (min)	0	1·0	3·0	5·0	15·0	30·0	∞ [a]
Λ [b]	10·4 [c]	13·5	22·3	27·1	36·9	41·8	50·1 [d]

$[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ ($10{\cdot}7{\cdot}10^{-4}$M) in CH_2Cl_2

Time (min)	0	15·0	∞ [a]
Λ [b]	16·4 [c]	42·2 [d]	45·0

$Pt(S_2COEt)_2$($10{\cdot}10^{-4}$M) + excess PPh_3 in CH_2Cl_2

Time (min)	0	0·25	0·5	1·0	3·0	15·0
Λ [b]	15·7	13·7	13·2	12·5	9·2	7·0

$Pt(S_2COEt)_2$ ($30{\cdot}0{\cdot}10^{-4}$M) + excess PPh_3 in CH_3NO_2

Time (min)	0	3·0	6·0	10·0	26·0	35·0	60
Λ [b]	90	80	71	61	50	33	19

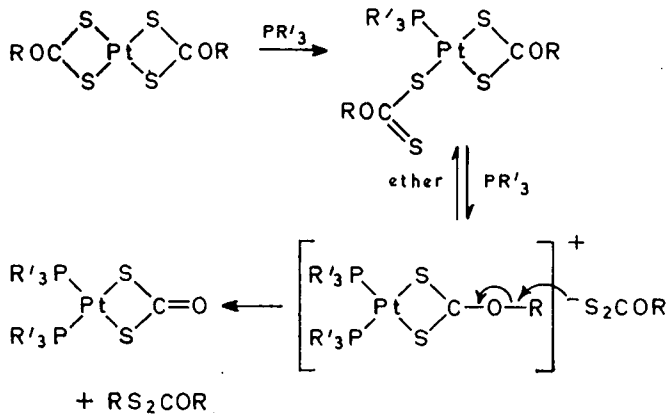
[a] 24 Hours. [b] In Ω^{-1} cm^2 mol^{-1}. [c] Yellow solution of $[Pt(S_2CNR_2)(PMePh_2)_2]S_2CNR_2$, $Pt(S_2CNR_2)_2(PMePh_2)$, and $PMePh_2$. [d] Decolourised solution containing $[Pt(S_2CNR)_2(PMePh_2)_2]Cl,H_2O$ and $CH_2(S_2CNR_2)_2$.

Xanthates and Dithiophosphates.—Reaction of $Pt(S_2P\{OEt\}_2)_2$ or $Pt(S_2COEt)_2$ with $PMePh_2$ (1 : 1 molar ratio) gives the compounds $[Pt(S{-}S)_2PMePh_2]$, originally formulated as five-co-ordinate species.[2,3] We suggest that these should be reformulated as four-co-ordinate compounds of type (III) on the basis of the detailed arguments given above for the related dithiocarbamate complexes. For comparison, we have made the triphenylphosphine and triphenylarsine analogues of these compounds and variable-temperature ^1H n.m.r. studies for $^-S_2P\{OEt\}_2$ parallel those reported earlier for the $PMePh_2$ derivative[3] (Tables 1 and 2). For $[Pt(S_2COEt)_2PPh_3]$ in CS_2, coalescence of the CH_3 triplet occurs at 188 K, but even at 173 K, the limiting spectrum has not been reached.

The reaction of either $M(S{-}S)_2$ or $[M(S{-}S)_2PR'_3]$ [M = Pt, Pd; $(S{-}S)^-$ = $^-S_2COEt$, $^-S_2COCH_2Ph$, $^-S_2P(OEt)_2$] with an excess of PR'_3 is of considerable interest. Fackler and Seidel[4] have studied the former in some detail and have convincingly demonstrated that the final products are the novel compounds $[(R'_3P)_2MS_2CO]$ (I) and $[(R'_3P)_2PdS_2P(O)OEt]$ (II) respectively and that for the xanthate reaction, xanthate esters are also formed. At that time, neither the detailed mechanism nor the role played by tertiary phosphines in these rearrangement reactions were understood. In this final section, we would therefore like to present evidence which rationalises these rearrangement reactions within the context of the overall mechanistic framework developed in this paper and in earlier work[1,6] for the reaction of platnum and palladium dithioacid complexes with tertiary phosphines.

We suggest that the reaction of platinum (or palladium) xanthates with PR'_3 is as given by the Scheme below, namely stepwise cleavage of metal–sulphur bonds to give the ionic 1 : 2 complex, followed by nucleophilic attack of the xanthate anion on the alkoxy-group of the co-ordinated xanthate to give the neutral dithiocarbonate complex and a xanthate ester. A similar scheme involving the ionic intermediate $[M(S_2P\{OEt\}_2)(PR'_3)_2]$-

($S_2P\{OEt\}_2$) would explain the formation of $[(R'_3P)_2MS_2P(O)(OEt)]$. This mechanism accounts for all the experimental observations made by Fackler and Seidel.[4] For example, the observation that platinum compounds undergo the rearrangement more readily than palladium and that carbon disulphide inhibits the reaction relative



SCHEME Proposed mechanism for reaction of $[Pt(S_2COR)_2]$ [R = Et, $PhCH_2$) with an excess of PR'_3

to chloroform is readily explicable in terms of the tendency of platinum to form the ionic 1 : 2 adducts more easily than palladium (*cf.* earlier S_2PPh_2 studies [1]) and the requirement of a fairly polar solvent to promote both the formation and stabilisation of the ionic intermediate. The fact that the ethyl group is eliminated less readily than the benzyl group is consistent with the greater stability of the benzylcarbonium ion generated in the transition state.

However, it is also possible to give more *direct* experimental proof for such a reaction scheme. On reaction of $Pt(S_2COEt)_2$ and an excess of PPh_3 in CH_2Cl_2, immediate decolouration, accompanied by a rapid increase in conductivity occurs (with a maximum value corresponding to *ca.* two-thirds of that expected for a 1 : 1 electrolyte). This is followed by a steady decrease and the isolation of (I) (Table 5). In nitromethane, the maximum value corresponds closely to that expected for a 1 : 1 electrolyte but again the readings decrease steadily with time (Table 5) and attempts to isolate the ionic species have been unsuccessful. For example, addition of an excess of light petroleum (b.p. 40—60 °C) within 20 s of mixing, give a precipitate of $[Pt(S_2COEt)_2PPh_3]$ together with a small amount of $[(PPh_3)_2PtS_2CO]$. This clearly demonstrates that both nucleophilic attack of $^-S_2COEt$ on a platinum–phosphorus bond and on a co-ordinated alkoxy-group are ready reactions. Presumably, lowering the polarity of the solution by addition of light petroleum facilitates attack on the metal. Although the ionic intermediate with xanthate as counter anion is too labile to be isolated, addition of $NaBPh_4$ to an acetone–methanol solution of $Pt(S_2COEt)_2$ and an excess of PPh_3 (within 30 s of mixing) gives a precipitate of $[Pt(S_2COEt)(PPh_3)_2]BPh_4$, which has been fully characterised by ^1H n.m.r., analysis, and conductivity measurements (Tables 1, 3, and 4).

Similarly, reaction of $Pt\{S_2P(OEt)_2\}_2$ with an excess of PPh_3 in CH_2Cl_2 produces rapid decolouration and the conductivity of the final solution corresponds to that of a 1 : 1 electrolyte (Table 3). Although in this instance, the conductivity readings are quite steady with time, all attempts to isolate the ionic species either by rapid removal of solvent or precipitation with diethyl ether have given only the rearranged product $[(PPh_3)_2Pt\text{-}S_2P(O)OEt)]$ together, in the latter case, with some $[Pt(S_2P\{OEt\}_2)_2PPh_3]$. However, it is possible to isolate and characterise $[Pt(S_2P\{OEt\}_2)(PPh_3)_2]BPh_4$ (Tables 1, 3, and 4) by addition of an excess of $NaBPh_4$ to an acetone–methanol mixture of the same reactants. It should be noted that for xanthate and dithiophosphate, there is no evidence here, or elsewhere,[18] for side-reactions with chlorinated solvents.

Conclusion.—Reaction of platinum (and palladium) dithioacid compounds with tertiary phosphines occurs by stepwise cleavage of metal–sulphur bonds to generate four-co-ordinate adducts of type (III) and (IV). For $(S\text{–}S)^- = {}^-S_2PR_2$ (R = Me, Et, Ph, and probably F), the ionic 1 : 2 compounds readily revert to the 1 : 1 compounds in nonpolar solvents by means of nucleophilic attack by $^-S_2PR_2$ on the metal. Similar processes occur for $^-S_2P(OEt)_2$, ^-S_2COR, and $^-S_2CNR_2$ but, in addition, competing nucleophilic attacks on a co-ordinated alkoxy-group occur with the first two anions and on chlorinated solvents (catalysed by free PR'_3) for the latter anion.

Although we have not investigated the dithiocarboxylate adducts reported earlier [2,3] the very recent brief mention of ' essentially planar PtS_3P co-ordination for $[Pt(S_2CC_6H_4\text{-}iPr)_2PPh_3]$ with the dangling sulphur atom 3·58 Å from the platinum(II) ion ' [19] [*cf.* in $Pd(S_2PPh_2)_2PPh_3]$ >3·5 Å away] [7] suggests these compounds also conform to the general pattern.

EXPERIMENTAL

Microanalyses were by the National Physical Laboratory, Teddington, A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. Analytical data for many of the new compounds are given in Table 4. I.r. spectra were recorded in the region 4000—200 cm^{-1} on a Perkin-Elmer 225 Grating Spectrometer, using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. ^1H N.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe. Mass spectra were measured on an A.E.I. MS9 mass spectrometer and conductivity measurements on a model 310 Portland Electronics conductivity bridge. Melting points were determined with a Köfler hot-stage microscope and are uncorrected.

Materials.—Potassium tetrachloroplatinate(II) and palladium(II) chloride (Johnson Matthey); triphenylphosphine, dimethylphenylphosphine, sodium diethyldithiocarbamate (B.D.H.); sodium dimethyldithiocarbamate (Ralph Emanuel). The other tertiary phosphines were prepared by standard literature methods.

[19] D. R. Swift, Ph.D. Thesis, Case Western Reserve University 1970, cited in J. P. Fackler, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 1009.

NN-Dialkyldithiocarbamate Complexes.—*Bis*(NN-*dimethyldithiocarbamate*)*platinum*(II). Potassium tetrachloroplatinate(II) in a minimum volume of hot water was mixed with an ethanolic solution of an excess of sodium *NN*-dimethyldithiocarbamate and shaken for 24 h. The yellow product was washed with water and ethanol and air-dried, m.p. 305—308° (Found: C, 16·8; H, 2·9; N, 6·3. Calc. for $C_6H_{12}N_2PtS_4$: C, 16·6; H, 2·8; N, 6·4%). *Bis*(NN-*diethyldithiocarbamate*)*platinum*(II) [20] (m.p. 245—250 °C) was prepared in the same way using K_2PtCl_4 and NaS_2CNEt_2-$3H_2O$.

Bis(NN-*dimethyldithiocarbamate*)*palladium* (II).[20] Palladium(II) acetate [21] was dissolved in benzene–dichloromethane and shaken for several hours with an ethanolic solution containing an excess of $NaS_2CNMe_2,2H_2O$. The yellow precipitate was filtered off, washed with water and ethanol, and air-dried (Found: C, 20·3; H, 3·3; N, 7·5. Calc. for $C_6H_{12}N_2PdS_4$: C, 20·8; H, 3·5; N, 8·1%).

Bis(NN-*diethyldithiocarbamato*)*triphenylphosphineplatinum*(II). Bis(*NN*-diethyldithiocarbamato)platinum(II) was suspended in carbon disulphide and treated with triphenylphosphine (<1 : 1 molar ratio). An orange-yellow solution was immediately formed, together with unchanged Pt-$(S_2CNEt_2)_2$; the later was removed by filtration. Partial removal of the solvent followed by cooling (200 K) gave the yellow crystalline *product*; this was washed with diethyl ether and dried *in vacuo*. *Bis*(NN-*diethyldithiocarbamato*)*methyldiphenylphosphine platinum*(II) was prepared in the same way, using a deficiency of $PMePh_2$ under nitrogen. Preparation of the PMe_2Ph compound was complicated by the side-reaction between the phosphine and CS_2.[22] These products are soluble in chloroform, dichloromethane, carbon disulphide, and benzene; and insoluble in ethanol, acetone, and dimethyl sulphoxide.

(NN-*Diethyldithiocarbamato*)*bis*(*methyldiphenylphosphine*)-*platinum*(II) NN-*Diethyldithiocarbamate*. $Pt(S_2CNEt_2)_2$ (0·90 mmol) in acetone (5 ml) was treated with an excess of methyldiphenylphosphine (1·0 ml, 4·0 mmol) to give an immediate yellow solution from which yellow crystals of the *product* rapidly separated. These were washed with light petroleum (b.p. 40—60°) and dried *in vacuo* (40 °C). (NN-*Dimethyldithiocarbamato*)*bis*(*methyldiphenylphosphine*)*platinum*(II) NN-*dimethyldithiocarbamate* was made by the same method. These compounds are very unstable, readily rearranging to form $[Pt(S_2CNR_2)_2(PMePh_2)]$ and free $PMePh_2$ on prolonged exposure to benzene, diethyl ether, or acetone. Attempts to make the corresponding triphenylphosphine and dimethylphenylphosphine ionic species were unsuccessful. The former gave only $[Pt(S_2CNEt_2)_2PPh_3]$ and the latter an intractable oil.

(NN-*Diethyldithiocarbamato*)*bis*(*methyldiphenylphosphine*)-*platinum*(II) *chloride monohydrate*. Method (A). $Pt(S_2CNEt_2)_2$ in dichloromethane (dried over $MgSO_4$) was treated with a three-fold excess of $PMePh_2$ under nitrogen. The initial yellow solution slowly became colourless (*ca.* 1—2 h) and concentration *in vacuo* followed by addition of an excess of diethyl ether gave a white microcrystalline precipitate of the *product*. This was washed with diethyl ether and dried *in vacuo* (40 °C).

Method (B). The same compound was also made by prolonged exposure of $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ to dichloromethane. The initial deep yellow solution slowly became colourless (*ca.* 2 h) and concentration of the solution followed by addition of an excess of diethyl ether gave the *product*. In addition, solvent removal from the ethereal filtrates in methods (A) or (B) gave an oil which, on trituration with light petroleum (b.p. 60—80°), gave a white crystalline *solid* characterised as *methylene bis*(NN-*diethyldithiocarbamate*), m.p. 70—71 °C [Found: C, 42·6; H, 7·2; N, 9·0. Calc. for $C_{11}H_{22}N_2S_4$: C, 42·6; H, 7·1; N, 9·0%]. Another method of preparation is to shake a mixture of $NaS_2CNEt_23H_2O$, dichloromethane (not scrupulously dried), and a tertiary phosphine (PPh_3, $PMePh_2$, or PMe_2Ph) for 24 h. Solvent removal and trituration of the resulting oil with light petroleum (b.p. 60—80°) gave the *product* characterised by m.p. and mass [18] and ^1H n.m.r. spectroscopy. The same compound was also formed (but in lower yield) when the reaction was carried out in the absence of PR'$_3$. Complexes $[Pt(S_2CNEt_2)(PR'_3)_2]Cl,H_2O$ (PR'$_3$ = PPh_3, $PMePh_2$) were also made by the procedure outlined in method (A), together with some $CH_2(S_2CNEt_2)_2$.

(NN-*Dimethyldithiocarbamato*)*bis*(*methyldiphenylphosphine*)*platinum*(II) *chloride monohydrate*. Method A. The method used was exactly as for the preparation of $[Pt(S_2CNEt_2)(PMePh_2)_2]ClH_2O$, using a suspension of $Pt(S_2CNMe_2)_2$ in dichloromethane and a three-fold excess of $PMePh_2$. Precipitation with either diethyl ether or light petroleum (b.p. 60—80 °C) gave a mixture of $[Pt(S_2CNMe_2)(PMePh_2)_2]Cl,H_2O$ and $CH_2(S_2CNMe_2)_2$. The latter was removed by careful washing with benzene, and the remaining crystalline *product* was washed with diethyl ether and dried *in vacuo* (40 °C). From the benzene washings, *methylenebis*(NN-*dimethyldithiocarbamate*) was isolated (m.p. 93—96°) [Found: C, 33·7; H, 5·3; N, 10·9. $C_7H_{14}N_2S_4$ requires C, 33·1; H, 5·1; N, 11·0%]. The compound was also made by shaking a mixture of NaS_2CNMe_2, CH_2Cl_2, and tertiary phosphine (PPh_3, $PMePh_2$, or PMe_2Ph); mass spectrum: 254 $[CH_2(S_2CNMe_2)_2^+]$, 166 $[Me_2NCS_2CH_2S^+]$, and 88 $[Me_2NCS^+]$ (*cf.* ref. 18).

In the absence of tertiary phosphine, only tetramethylthiuram disulphide (Found: C, 31·3; H, 5·2; N, 11·9. Calc. for $C_6H_{12}N_2S_4$: C, 30·0; H, 5·0; N, 11·7%) and NaS_2CNMe_2 were detected.

Method (B). From $[Pt(S_2CNMe_2)(PMePh_2)_2]S_2CNMe_2$ dissolved in CH_2Cl_2, the deep yellow solution slowly becoming colourless. Precipitation with diethyl ether and extraction of $CH_2(S_2CNMe_2)_2$ with benzene gave the white *product*.

$[Pt(S_2CNMe_2)(PR'_3)_2]Cl,H_2O$ (PR'$_3$ = PPh_3, PMe_2Ph, $PEtPh_2$) and $[Pd(S_2CNMe_2)(PMe_2Ph)_2]Cl,2H_2O$ were also made by the procedure outlined in method (A), together with some $CH_2(S_2CNMe_2)_2$.

(NN-*Diethyldithiocarbamato*)*bis*(*methyldiphenylphosphine*)*platinum*(II) *tetraphenylborate*. $[Pt(S_2CNEt_2)(PMePh_2)_2]Cl,H_2O$ was dissolved in methanol and treated with a concentrated acetone solution of $NaBPh_4$. The white precipitate of the *product* was washed with water and light petroleum (b.p. 60—80 °C) and dried *in vacuo* (40 °C). The same compound was also obtained by reaction between $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ and $NaBPh_4$ in ethanol.

Similarly, the complexes $[Pt(S_2CNR_2)(PR'_3)_2]BPh_4$ (R = Me, Et; PR'$_3$ = PPh_3, PMe_2Ph, $PEtPh_2$) were prepared from $[Pt(S_2CNR_2)(PR'_3)_2]Cl,H_2O$ and an excess of $NaBPh_4$.

(NN-*Diethyldithiocarbamato*)*bis*(*methyldiphenylphosphine*)-*platinum*(II) *hexafluorophosphate*. $[Pt(S_2CNEt_2)(PMePh_2)_2]$-

[20] C. K. Jorgensen, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1571.
[21] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.
[22] See L. Maier in *Progr. Inorg. Chem.*, 1963, **5**, 129.

Cl,H_2O in acetone–methanol was added to an aqueous solution of ammonium hexafluorophosphate to give a white colloidal precipitate. Partial removal of solvent *in vacuo* gave a white *powder* which was washed with water and light petroleum (b.p. 60—80°) and dried *in vacuo* (40 °C). $[Pt(S_2CNMe_2)(PMePh_2)_2]PF_6$ and $[Pt(S_2CNEt_2)(PPh_3)_2]PF_6$ were also prepared by this method.

OO'-Diethyl Dithiophosphate Complexes.—*Bis*(*OO'-diethyl dithiophosphate*)*platinum*(II) was prepared as described earlier (m.p. 124 °C) [20] (Found: C, 17·2; H, 3·5. Calc. for $C_8H_{20}O_4P_2PtS_4$: C, 17·0; H, 3·6%).

Bis(*OO'-diethyl dithiophosphate*)(*triphenylphosphine*)*platinum*(II). $Pt[S_2P(OEt)_2]_2$ was shaken with triphenylphosphine (1 : 1 molar ratio) in dichloromethane to give a lemon-yellow solution. Slow evaporation of the solvent in the presence of an excess of light petroleum (b.p. 40—60°) gave yellow crystals of the *product*. $[Pt\{S_2P(OEt)_2\}_2AsPh_3]$ was prepared *in situ* by reaction of $Pt\{S_2P(OEt)_2\}_2$ and an excess of $AsPh_3$ in $CDCl_3$.

O-*Ethyl dithiophosphatobis*(*triphenylphosphine*)*platinum*(II). $Pt\{S_2P(OEt)_2\}_2$ and PPh_3 (*ca.* 1 : 3 molar ratios) were refluxed in $CHCl_3$ for *ca.* 3 h during which time the initial yellow solution slowly became colourless. Removal of solvent and addition of diethyl ether gave a white *product*. Reaction of $Pt\{S_2P(OEt)_2\}_2$ and an excess of PPh_3 in CH_2Cl_2 rapidly gave a colourless conducting solution, presumably containing the ionic $[Pt\{S_2P(OEt)_2\}(PPh_3)_2]S_2P(OEt)_2$, but removal of solvent by a stream of nitrogen and washing with light petroleum (b.p. 40—60 °C) was sufficient to cause rearrangement to $[(PPh_3)_2Pt(S_2P(O)OEt)]$.

(*OO'-Diethyl dithiophosphate*)*bis*(*triphenylphosphine*)*platinum*(II) *tetraphenylborate*. $[Pt\{S_2P(OEt)_2\}_2]$ in methanol was treated with an excess of triphenylphosphine in a minimum volume of acetone, followed by addition of an aqueous solution of $NaBPh_4$. The white *precipitate* was well washed with water and diethyl ether and dried *in vacuo* (40 °C).

O-*Ethyl Dithiocarbonate Complexes.*—Bis(O-*ethyl dithiocarbonato*)*triphenylphosphineplatinum*(II). $Pt(S_2COEt)_2$ [23] and PPh_3 (1 : 1 molar ratio) were shaken in a minimum volume of $CHCl_3$ to give a lemon-yellow solution. Trituration with an excess of light petroleum (b.p. 40—60 °C) gave a pale yellow crystalline precipitate which was washed with diethyl ether and dried *in vacuo* (40 °C). The same product (contaminated with a small amount of $[Pt(S_2CO)(PPh_3)_2]$) was also obtained by reaction of $Pt(S_2COEt)_2$ with an excess of PPh_3 in CH_2Cl_2 followed by immediate addition of an excess of light petroleum (b.p. 40—60 °C).

(*Dithiocarbonate*)*bis*(*triphenylphosphine*)*platinum*(II)–*chloroform*. $Pt(S_2COEt)_2$ was shaken with an excess of PPh_3 in dichloromethane to give a colourless conducting solution. Partial removal of solvent and addition of light petroleum (b.p. 60—80 °C) gave a white *product*, which was non-conducting when redissolved in CH_2Cl_2 (m.p. 256 °C) [Found: C, 49·2; H, 3·3. Calc. for $C_{38}H_{31}Cl_3OP_2PtS_2$: C, 49·1; H, 3·3%].

O-*Ethyl dithiocarbonatobis*(*triphenylphosphine*)*platinum*(II) *tetraphenylborate*. $Pt(S_2COEt)_2$ in acetone–methanol was treated with an excess of PPh_3 in a minimum volume of acetone, followed immediately by addition of an aqueous solution of $NaBPh_4$. The resulting white *precipitate* was well washed with water and diethyl ether and dried *in vacuo* (40 °C).

We thank Johnson–Matthey Ltd. for loans of potassium tetrachloroplatinate(II) and palladium(II) chloride, the S.R.C. for an award (to J. M. C. A.), Professor J. I. G. Cadogan, Dr. R. O. Gould, and Dr. D. Leaver for helpful discussions, and Mrs. M. Groves and Mr. J. Miller for obtaining the variable-temperature ^1H n.m.r. spectra.

[2/1443 *Received*, 21*st June*, 1972]

[23] C. W. Watt and B. J. McCormick, *J. Inorg. Nuclear Chem.*, 1965, **27**, 898.